

CHARACTER OF 1,1,1,3,3,3-HEXAFLUORO-
[2,2]PARACYCLOPHANE: ITS SYNTHESIS AND REACTIONS

By

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*Abstract of Dissertation Presented to the Graduate School
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Requirement for the Degree of Doctor of Philosophy*

**CHEMISTRY OF 1,1,1,3,3,3-HEXAFLUORO-
[2,2]PARACYCLOPHANE: ITS SYNTHESIS AND REACTIONS**

By

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This dissertation describes the first example of the synthesis of 1,1,1,3,3,3-hexafluoro[2,2]paracyclophane (APF) under non-high-pressure conditions. Under very mild reaction conditions, hexa-fluoroisobutene-trifluoromethane (TFPX dibromide) and its derivatives reacted with Fe dust in N,N-dimethyl acetamide (DMA) (Ziegler method) affording the corresponding APF and its derivatives in moderate to good yields. Purification of products was also studied and an efficient purification process was developed.

A new and very simple method for the preparation of TFPX dibromide is also described. Using the very strong fluorinating reagent, antimony hydrogen fluoride (AHF), 1,3-hexafluoroisobutene-trifluoromethane or its derivatives were converted to TFPX and

in derivatives in high yields (FICI exchange reaction). With the success of the first method and FICI exchange reaction, highly pure AP4 that can be provided to the semiconductor industry and academy research community in large quantity and at a very low price.

Starting from AP4, numerous AP4 derivatives were synthesized using conventional reaction conditions. Reaction of AP4 with thiolating reagents under microwave gave mono-*ortho*-AP4 in almost quantitative yield. Reduction of the mono-*ortho*-AP4 with iron powder in the presence of HCl in acetic acid solvent gave the diene-AP4 in 80% yield. Via the diene-AP4 unit, intermediates, *ortho*-AP4 was also obtained in good yield. Under similar reaction conditions, chloromethylated AP4 derivatives were also prepared in good yields.

Heating a mixture of AP4, trifluoromethyl peroxide and dichloromethane gave the trifluoromethylated diene AP4 as a mixture of diastereomers. When these products were heated in 170–180°C in the presence of I_2 , 4-trifluoromethyl-AP4 was obtained in almost 85% yield. X-ray structural analysis showed that the C–C bond connecting the two cyclopentadiene moieties to be longer than the normal C–C bond. Kinetic studies, conducted in the presence of excess amount of hydrogen donor, showed the bond to be quite weak.

Oxidation of AP4 with H_2O_2 in the presence of catalytic amount of H_2SO_4 in trifluoroacetic acid gave AP4 quinoxaline in one step. AP4 quinoxaline can be easily reduced to the hydroquinone by $Na_2S_2O_4$ aqueous solution.

CHAPTER 1 AN OVERVIEW DEVELOPMENT OF THE CHEMISTRY OF [2,2]PARACYCLOPHANE AND ITS

1.1 Introduction

1.1.1 History of [2,2]Cyclophane

The first cyclophane was synthesized by Pedersen in 1950. Starting from 1,2-bis(bromomethyl)benzene **1**, he successfully prepared the [2,2]-metacyclophane **2** by a Wurtz coupling reaction (Scheme 1).¹



Scheme 1

The "Age of cyclophane" actually begins in 1955 with the first synthesis of [2,2]paracyclophane **3** by Brown and Furlong.² They obtained **3** by extraction from pyrolysis products of *p*-xylene **4**, such pyrolysis first having been described by Szwarc.³ Brown and Furlong were published a few months later together structural analysis (Scheme 2).



Figure 1. Components of cyclophane: aromatic nucleus (benzene or naphthalene) and an aliphatic bridge.

This cyclophaneomenclature was further systematized and extended by Virgil and Newman.² In place of the generic heading cyclophane they chose the class designation "phane", which describes all bridged aromatics (including condensed and heteroaromatic such as naphthalene and pyridine). The prefix "cyclo" thus stands for the aromatic rings. As the literature mainly deals with (2,2)paracyclophane, more accurately the bridge perforated (2,2)paracyclophane derivatives, discussion will thus mainly focus on the (2,2)paracyclophane. The structure of (2,2)paracyclophane is shown as follows.



Figure 2. The structure of (2,2)paracyclophane.

The numbers in square brackets stand for the bridge length, and para means the 1,4-substitution on the aromatic ring, for (2,2)paracyclophane thus can also be named [(2,2)-4,4]cyclophane.

1.1.1 Why Cyclophane Chemistry

In his first publication on cyclophanes [1] Ito had already expressed his opinion about some problems to be expected in cyclophanes, which he outlined as follows:

- electronic interaction between aromatic rings placed "face-to-face",
- the resulting influence on substitution reactions in the aromatic rings; i.e., influence of substitution in one ring through-transcyclic electronic effects, which are reduced by other ring,
- intermolecular charge-transfer interactions,
- ring strain, steric strain, transannular strain

These problems have been subsequently substantiated extensively. From studies it has been demonstrated that aromatic rings in many cyclophanes are not planar, but are distorted out of planarity through bending (front and backside between rings)¹ it has been shown unequivocally by X-ray structure analysis that benzene rings can be distorted in front, clear, and front-back by clamping or bridging them in cyclophane structures. These stereochemical distortions create spectroscopic and chemical consequences, which are of interest to all chemists, particularly in connection with kinetics, equilibria, reaction, reaction

Tightly "clamped" cyclophanes are typically strained, the ring strain results in various or highly strained molecules such as [6]paracyclophane, available through a direct synthesis. The question arises as to what extent benzene rings can be bent and distorted and what the resulting spectroscopic and chemical consequences are. How closely can benzene rings be pressed face-to-face, and what modifications with respect to spectroscopy and chemical reactivity result?



(p-terphenylene)

What influences does distance of aryl rings have on the "transmission"? With the construction of molecules with several benzene rings linked in a straight fashion, it should be possible to study trans-molecular electronic and steric effects transmitted through more than two rings. Benzene rings can indeed be arranged into multi-layer cyclophanes, and trans-molecular electronic effects through more than two aromatic rings can be detected spectroscopically. Furthermore, planar molecules can orient themselves in planar, chiral and helical arrangements, and the resulting arrangements, once repeated, have been examined with respect to their chiroptical properties.

Another consideration in the placement of "intramolecular" substituents are the steric opening of the cyclophane. This increases the existing steric strain, employed in van der Waals interaction between the protruding groups or substituents inside the cavity.

What conformations do cyclophanes assume? Which of these are favored? How are dihydrolic chains arranged between the aromatic rings? How flexible are such chains and aromatic rings? How is flexibility altered by length of the bridge and substituents on the aromatic ring? How is the strain energy in larger cyclophane molecules distributed among various groups? Can strained cyclophanes serve as synthons for the preparation of other molecules? In the case of the head-to-head arrangement of arylbenzenes, the question

mean as to whether photochemical and topochemical (in the crystal) reactions might be interconvertible.

All these questions make it clear that phthalones are ideal model compounds, in which benzene and other aromatic rings can be placed relative to one another in rather facile fashion. Bridged cyclophanes are often rigidly symmetric, and so convenient subjects for spectroscopic experiments.

With cyclophane chemistry one has the opportunity gradually and systematically to increase the distances. Consideration of extended systems such as anthracene, decalone, dibenzo-decalone, etc. makes it clear that changes in the aromatic ring will affect the spectroscopic experiments.

With the phthalene structure it is possible to place interesting fluoromethyl bridging units close to the aromatic ring, for example to incorporate a dimethyl fluor-to-fluor bridge over benzene rings. In this way one can achieve a particular arrangement of functional groups and thereby trigger their chemical interactions.

Although cyclophanes were first considered as model and synthetic, there being no thought toward their industrial applications, the situation has changed completely. With the possibility of locating groups precisely in space, cyclophane chemistry has provided the building and the units, in their various, "multi-line structures" helices, macrocyclics, macro-benzoverides (novel ligand systems, etc. Cyclophane chemistry has become a major component of supramolecular chemistry, of molecular recognition, of models for intercalation, of the building blocks for organic catalysts, receptor units, crown ethers, and organogels.¹²

Cyclophane chemistry has proved to represent a large variety of molecules and processes. It is the wide variety of arrangements of formal structures, bond or conformationally flexible, that affords such a rich field for research into molecular design, synthesis, structural analysis, physical investigations, chemical reactions, and all the way to supramolecular chemistry.

1.1.4 Structural Characteristics and Special Reactivity of [1,1]Phenacyclophanes

Because [1,1]phenacyclophane in particular affects the chemistry of cyclophanes to a significant extent,¹¹ it can be considered as the key member or the very essence of cyclophane chemistry. The two essential characteristics of [1,1]phenacyclophane are the interaction between the π electron systems of the two benzene ring phases ("the dimer") and the deformation of the benzene rings, together with the consequences that result. These characteristics are manifested as anomalous directing effects in higher electrophilic substitution, neighboring group effects of the [1,1]phenacyclophane unit, *cis* addition at the diphenylbridges as well as isomerization, recombination, and photochemical reactions of [1,1]phenacyclophanes and their analogues. For the reason the [1,1]phenacyclophane have provided chemists with a challenging domain with which to try to quantify these complicated electronic and steric effects.

The interaction between the π systems of the two benzene rings in [1,1]phenacyclophane leads to novel, extended π systems spread over both rings, whose highest occupied molecular orbital (HOMO) is higher than that of the corresponding ethylenicene monomeric compound. Its lowest unoccupied molecular orbital (LUMO)

lies at a lower level than that in the open chain reference molecule. The doubling of the molecular weight and narrowing of the HOMO-LUMO energy gap by comparison to benzene reflect direct consequences on the chemical and physical properties of the [2] *thianthrylphthalene*. The same type of interaction, albeit weaker, exists in the [2] *thiopyrroline* but is absent in the more widely separated [4-4] *pyridophthalene*, where the individual benzene rings behave as separated isolated electronic systems. With the availability of X-ray crystallographic analysis for representation of concrete spatial relationships and of a variety of approaches in MO theory, the quantification of intermolecular interactions and the precise significance of their contribution have become an ongoing problem in chemical research.

A number of X-ray crystal structure analyses of [2] *thianthrylphthalene* have been reported. They show that the four aromatic bridging atoms (C(3), C(3'), C(2) (4), and C(2) (4')) are displaced out of the planes of the remaining benzene carbon atoms, with the result that the aromatic rings are deformed into boat-like shapes.



The intramolecular separation between the central carbon atoms of the two benzene rings is displaced to 3.20 Å (The normal van der Waals separation between parallel benzene rings is about 3.40 Å as a minimum.)

The shortening is attributed to a considerable transannular $\pi-\pi$ overlap, with the consequent reduction in the separation between the bridging atoms to only 3.71-3.77 Å. As compensation for the effects of the transannular steric and electronic interaction, the

CN₂-CN₂ bond length in the bridge is unusually large: 1.43 Å (at 294 K), 1.39–1.50 Å.

(X-ray crystal structure analysis at 10 K)

Reyn¹² estimated the strain energy (SE) in the [2,2]paracyclophane molecule at [29–31 kJ/mol]. Although the strain is distributed throughout the molecule's framework, the largest strain resides in the distortion of the benzene rings from planarity.

1.2 Relationship of the Reactivity and the Structure

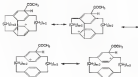
1.2.1 Transannular Directing Effect in Electrophilic Aromatic Substitution¹³

Besides intermolecular chemical reactions leading to new bonds, there are also certain chemical transformations within [2,2]paracyclophane series which manifest themselves in the formation of charge transfer complexes between two aromatic rings. Transannular effects within [2,2]paracyclophane series are characterized by the strong electronic effect exerted by one aromatic ring in the course of reactions taking place in the other aromatic ring. The strong dependence of transannular interactions on molecular geometry is evident.

Determination of the relative rates of acylation in the [n,2]paracyclophane series reveals a remarkable situation. While the rate for [2,2]paracyclophane (ac⁺ac⁻) is set as 1, the relative rates for the following paracyclophane are

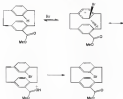
[4,4]paracyclophane	1.6
[4,3]paracyclophane	11
[2,3]paracyclophane	>40

Thus, the closer the benzenic rings are to each other, the more easily the rate rises for the incorporation of the first aryl group. These observations clearly support the involvement of an intermediate **X** for monosubstitution in which the partial positive charge is distributed over both benzenic rings (Scheme 4).



Scheme 4

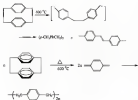
When there is one substituent on one aromatic ring, it will affect the reactivity and regio selectivity of the other ring due to the unique geometry of [1,1]paracyclophanes. The most striking example of such transannular directing effect is provided by the existence of predominant pseudo-para- or pseudo-ortho-substitution or introduction of [1,1]paracyclophanes containing basic substituents (carbonyl, amine, acyl, amide). The oxygen atom of the functional group is favorably inclined to accept a proton from the pseudo-para- or pseudo-ortho position in the examples.



Reference 5

3.3.3 Thermal Isomerization and Reversion

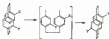
The high strain energy in [2,2]paracyclophane facilitates ring opening by cleavage at the bridge position. Pyrolysis at 400 °C leads to *o*-*o'*-dicyanophenyl and *o*,*o'*-dicyanobiphenyl. At 400 °C *p*-xylylene is generated, and it polymerizes to poly(*p*-xylylene).¹⁶



Scheme 4

The analysis of [2,2]paracyclophane at 300 °C is a very important reaction, and based on this reaction, Nakaya has used [2,2]paracyclophane as CVD precursor.

When p -4-methoxycarbonyl [2,2]paracyclophane is heated at 300 °C, it undergoes conversion without decomposition, the rate being relatively insensitive to solvent polarity (benzyl, toluene, *n*-hexane). Because of the rigid ring structure, isomerization can only proceed by a ring opening followed by a recombination. The activation energy for the process was determined to be 139 kJ/mol³⁴. By studying the thermal conversion of a variety of disubstituted [2,2]paracyclophane at 300 °C, Borch and Criss concluded that the isomerization proceeded through the disubstituted intermediates.



Scheme 1

1.1 Structural Characteristics and Synthesis of Bridge Fluorinated [2,2]Paracyclophane

Organic fluorine chemistry is a subject of comparatively recent growth, because very few of its compounds occur naturally and no relatively simple reagent exist for the synthesis of C-F bonds. The subject beginning can be traced back to France, where Courtois and Pelletier adopted what seems to have been the first recorded synthesis of an organic fluoride (methyl fluoride) as HCl (used as hydrogen) ¹⁸ It is well accepted that fluorine chemistry started from 1908 when Miesner first isolated elemental fluorine F_2 .¹⁹ From the very beginning organicfluorine chemists have concentrated themselves to find new materials with special properties because of the unique characteristics of the fluorinated organic compounds.

The substituentfluorine bond is a strong one, as the data in table 1 show.¹⁴ Further, the strength of such C-F bond increases with a decrease in the number of fluorine atoms on the carbon backbone.¹⁷ The overall size of fluorine as a substituent is also important [van der Waals radius is $\sim 1.35 \text{ \AA}$ (Coulson) $1.2 \text{ \AA}$]. It is possible to put all the fluorine necessary to produce a saturated fluorocarbon chain or ring system without significant overcrowding (an analogous fluorine is not compatible with the other halogens), however,

the carbon backbone is extremely well shielded. Lastly, and most importantly, fluorine is the most electronegative element (H 2.1, C 2.5, O 3.5, F 4.0 on Pauling's scale) and it alters the electron density, inductivity, and reactivity of neighboring groups.

Table 1. Bond Lengths and Energies in Polysulfonamides.¹²

Structure	S = O		S = SO ₂		S = SO ₃	
	Si(C-F) Å	Si(C-F) kcal/mole	Si(C-SO ₂) Å	Si(C-SO ₂) kcal/mole	Si(C-SO ₃) Å	Si(C-SO ₃) kcal/mole
C-H-S	1.333	107.5	1.332	79.8	1.328	66.6
C-H-S ₂	1.338	109.6	1.331	77.9	1.318	66.6
C-H-S ₃	1.342	111.7	1.301	76.1	1.300	65.1
C-S	1.317	108.8	1.368	70.7	1.342	66.6

Concomitant with an increased understanding of the behavior of organosulfonate compounds, considerable progress has been made in the development of new synthetic methodologies.¹⁷ In our laboratory, considerable efforts have been expended on the development of a commercially acceptable way to synthesize 1,1,2,2,5,5,10,10-octafluoro-2,2[paracyclophane] (AF4).

[2,2]paracyclophane has been recognized since the mid-1970s to be useful chemical vapor deposition (CVD) precursors of thin film polymers known as the polyimide "polyimide" ¹⁸ but, polyimides are already noted for use as molecular coatings in a wide variety of applications such as in the electronics, semiconductor, automotive, and medical industries. Polyimide coatings are thin, and transparent, and have excellent thermal properties. Polyimide IV, which is generated from the parent hydrocarbon I, has been found to be useful at temperatures up to 130 °C.

The structure of 1,1,1,2,5,5,10,10-octafluoro-2,2[paracyclophane] (AF4) is fully bridge fluorinated version of [2,2]paracyclophane is very similar to that of the

(2,2)paracyclophane. The X-ray structure of AP4 was reported 20 years ago.¹² Some key structural data are listed in Table 2 for comparison.

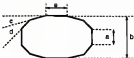
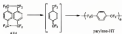


Figure 1. Structural parameters of (2,2)paracyclophane system.

Table 2. Comparison of Structural Features of AP4 and (2,2)paracyclophane

	(2,2)paracyclophane	AP4
$a(\text{\AA})$	1.605	1.511
$b(\text{\AA})$	3.395	3.365
$c(\text{\AA})$	12.4	11.8
$d(\text{\AA})$	11.3	12.0
$z(\text{\AA})$	1.494	1.395

AP4 has been proved to be a C₂H₂ precursor to form the so-called parylene-IT polymer, poly(p,p',p'',p'''-tetrafluoro-p-ylene).¹³



Scheme 6

The Polyimide-PII polymer contains a low dielectric constant ($2.25^{[2]}$) with high thermal stability (>1 with low T_{max} at 400 °C), low moisture absorption ($<0.1\%$), and other advantageous properties^[3,4] with such properties and because its structure depends greatly on the conformation of the aromatic backbone and superior electronic gap filling capability, Polyimide-PII continues to show considerable promise as an insulating material for on-chip high-speed semiconductor device interconnection.

The unique properties of PII also derive from the substitution of CF_3 with CF_2 . Especially when the fluoro- or fluorinated functional groups are incorporated into the materials, the properties will change a lot due to the following reasons:

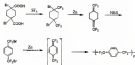
- A. The fluorination of organic compounds always results in low surface energy because of the incompatibility of the fluorination with other organic compounds or water, that is, the fluorinated films PII has very low moisture absorption.
- B. The strong C-F bond inhibits the reactivity of the fluorinated compounds, thus enhancing their stability.
- C. Fluorination of the aliphatic chain gives a symmetrical or balanced structure having molecule dipole character and low polarizability. This leads to a relatively low dielectric constant.

The research on the synthesis of bridge-fluorinated 1,1'-biphenyls is mainly driven by the semi-conductor industrial need for the low dielectric constant materials. Decreasing the dielectric constant ($\epsilon_r < 1$) while still keeping a high thermal stability (>400 °C) are the two most important properties of the interconnect materials required by SEMATECH to solve the problem of RC delay for ultrahigh speed

integration (IR, NMR) technology²² To modify the material as well as the process needs, chemical vapor-deposited polymers (e.g., polyenes) have been intensely investigated.²³

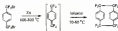
Even though other partially fluorinated 1,1'-biphenylolanes have been synthesized, AP4 has proven to be the best one.²⁴

The first synthesis of AP4 polymer was the result of attempts to study the stability of *s, s, s', s'*-tetrafluorobiphenylene. When Martin passed the steam of 1,4-bis(trifluoromethyl)benzene through a heated pyrex tube filled with zinc or zinc-copper couple a white polymer was obtained in the trap at -70 °C, as AP4 dimer was detected.²⁵



Scheme 1

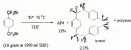
By modifying the reaction conditions of pyrexolane acetone from Green Carbide could obtain AP4 dimer in 7-22% yield.²⁶ Different from the first method, a large amount of solvent was used to dilute the concentration of tetrafluorobiphenylene, thus, when the thermal intermediate was formed it had enough time to cyclize before another monomer was added to react with the reactive intermediates.



Scheme 10

Although the pyrolysis of the dimethyl-diol gave AP4 cleaner under appropriate reaction conditions, the harsh reaction conditions prevents it being used in the common organic synthesis process and it could not be scaled up, thus this process could not provide AP4 in a commercial way.

In 1993 another method was reported from this lab. Under moderate reaction conditions, AP4 could be obtained in 40% yield in small scale, however, when the reaction was scaled up to a 50 gram scale, only oligomers and polymers were obtained (Scheme 11).²⁷



Scheme 11

Further effort resulted in another method which was scaled up to kilogram scale (3.40% yield)²⁶



(100 gram in 10 L solvent)

Scheme 12

The drawback for the industrial application is the use of the strong reducing agent: $(n\text{-Bu}_4)_2\text{SnCl}_2$ and expensive $n\text{-BuLi}$. Also the lack of easy preparation of the fibrous materials prevents its commercial application.

The major goal of this dissertation is to develop a cheap and easy scale-up procedure to produce API and its derivatives.

CHAPTER 2
A NOVEL, NON-SOLVENT-COULTRON METHOD FOR
PREPARATION OF AP4 AND ITS DERIVATIVES

2.1 The Preparation and Purification of AP4

2.1.1 Introduction

Since their first designed synthesis in 1944,¹⁻³ [2,2]paracyclophanes have been considered valuable compounds for testing the theories of bonding, ring strain, and π -electronic interactions.^{12-26, 31} A number of methods have been devised for the relatively convenient synthesis of paracyclophanes, all of which require the use of high dilution methodology.¹⁹⁻²⁴

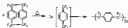


[2,2]paracyclophane

In addition, it has been recognized since the mid-1970s that [2,2]paracyclophanes are useful chemical vapor deposition (CVD) precursors of thin film polymers, known in the industry as "parylene".²⁷⁻²⁹ Such parylenes are widely used for use as conformal coatings in a wide variety of applications such as in the electronics, semiconductor, automotive, and medical industries. Parylene-coatings are neat and transparent and have excellent

thermal properties. Phthalic N, which is generated from the parent hydrocarbon **1**, has been found to be useful at temperatures up to 120 °C.

1,1,2,2,3,3,6,6,8,8-Decabenz[2,2]paracyclophane, **3**,²² the bridge-fluorinated version of **1** (and known in the industry as AP4), is the CVD precursor of Phthalic-BB polymer.^{23,24} The synthesis of AP4 at reasonable cost is thousands of years ahead.

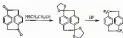


Scheme 1

The synthesis of fluorinated compounds can be realized by two general strategies:

A functional group transformation, in this way a carefully designed starting material will selectively react with fluorinating reagents, such as HF,^{25,26} SF₆,²⁷ SO₂/CHF₃, (DAAT),^{28,29} is the synthesis of bridge-fluorinated [2,2]paracyclophane, such strategy was used to synthesize hexafluoro[2,2]paracyclophane.

In 1999 Itoh reported³⁰ the synthesis of 1,1,3,3-tetrafluoro[2,2]paracyclophane starting from 1,3-difluoro[2,2]paracyclophane by two steps:



Scheme 2

Very recently Stange disclosed another method for the synthesis of two tetrafluoro(1,12)paracyclophane isomers in two steps starting from (1,2,7,8)paracyclophane.⁴⁰



Scheme 1

Even though the partially fluorinated (1,12)paracyclophanes were synthesized through their functionalized transformations, C_{12}F_4 has not been synthesizably such methodology.

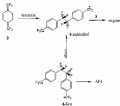
■ Starting from fluorinated building blocks, partially or fully fluorinated starting materials can be prepared using various synthetic methodologies. The efficiency of such methods generally depends on the availability of the building blocks as well as upon development of methods for replacing them. With the advance of organofluorine chemistry more and more fluorinated reagents will be available than paraffin elements were chosen. This is a very active current area of research.

All the reported methods for the synthesis of AP4 use strategy II with the “building block” being tetrafluorocyclophane **3**:



Because tetrafluorocyclophane is very reactive, it will react with another such molecule to form the dimeric divinyl intermediate **4** and the divinyl intermediates will either undergo ring-closures or react with another tetrafluorocyclophane to eventually form oligomers or polymers. The success of preparation of AP4 depends mainly on whether tetrafluorocyclophane can be produced in such a slow rate that it allows the divinyl **4** to ring close to form the desired AP4 before it has the chance to encounter another tetrafluorocyclophane or proceed down the oligomeric path (Scheme 3).

Particular, a significant aspect of methods for synthesis of virtually every [2,2]paracyclophane has been the necessity to carry out such reactions using high dilution conditions.^{17-20,22} Use of high dilution conditions is generally required in such processes in order to provide the optimal kinetic environment to allow intramolecular cyclization of intermediate divinyl **3** to compete effectively with undesired bimolecular oligomerization.



Scheme 3

Nonetheless, a significant aspect of methods for synthesis of virtually every [2,2]photocyclophane has been the necessity to carry out such reactions using high dilution conditions.^{10,11,12} Use of high dilution conditions is generally required in such processes in order to provide the optimal kinetic environment to allow unimolecular cyclization of intermediate derived **2** to compete effectively with undesired bimolecular oligomerization.

To make the process of preparing **4-CPA** commercially feasible, it is necessary that a simple and more suitable process be found, and this was the central goal of our research.

Again significantly, the use of lithium promoters, if indeed is essential to the success of both the TP and carbene promoted, was not required for this synthesis, and its use in place of lithium 2 leads to a greatly diminished (<10%) yield of AP4 along with a lot of unidentified side products.

The use of zinc dust (purity: Catalogue number 19074-0040) gave the best result, the use of other reducing agents gave poor conversion or poor yields. The size and the purity of the zinc dust are also important to the success of the reaction. For example, cheap, 99.99% zinc powder (100 mesh) can not initiate the reaction, only the starting material are recovered. The presence of Cu inhibits the reaction completely.

Only polar solvents work for this reaction. When non-polar solvents, such as benzene, toluene are used, no reaction occurs. The use of DMSO, gives the best result, though the use of a mixed solvent such as DMA/CN-CN makes the reaction even shorter and decreases the generation of the reduced and dehalogenated products 4 and 5. The use of non-polar solvents, DMSO, DMF and N-methyl pyrrolidone increases the rate of 4 and 5 to AP4.

Since the reaction is a heterogeneous one, the speed of stirring is essential to the success of the reaction. A lower stirring speed results in a lower yield as well as lower conversion of starting material.

When nitroacetylenediol (polymer ¹⁸) which has very strong reduction potential in Zn, is used, the reaction affords only 1% AP4 (estimated by ¹³C NMR) with 100% conversion even though the reaction is homogeneous. The main side product is 1,4-bis(4-bromomethyl)benzene 9.



Scheme 8

The ratio of AP4 in the reduced products (6 + 7) does not change during the course of the reaction. Treatment of pure AP4 with Zn powder under similar reaction conditions for 20 hr leads to reduction of AP4 and AP4 is recovered completely. These results may indicate that AP4 is formed on the surface of Zn powder. Increasing the molar ratio of Zn powder to the disulfide also reduces the reaction time to 4 hrs without affecting the yield of the AP4. When zinc was used as the reducing agent, no difluoromethylated benzene derivatives were detected in ^{19}F NMR.

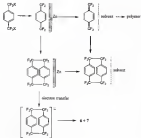
Even though the use of acid-treated zinc powder does not change the reaction yield, on the large scale reaction (1 T kg scale) the addition of I_2 to activate Zn in situ decreases the activation period from 4 hr to ca. 30 min.

To test the solvent a second batch of disulfide and zinc powder could be added to the previous batched reaction mixture. No induction period was observed, but the reduction of the product became impossible due to the decomposition of the solvent, even though from the ^{19}F NMR the reaction yield did not change.

When THF was used as the solvent, after 72 hr refluxing under H_2 a mixture with the almost 4 as the major product was obtained.

2.1.3.3. Possible Reaction Mechanism

As the reaction is initiated by the presence of O_2 , the initial step for the reaction may be electron transfer from Zn to dichloride. The dichloride accepts two electrons from Zn to form antiheteropentaplexon **3** on the surface of Zn. Since the ratio of AP4 to $(\text{R} + \text{T})$ does not change during the course of the reaction, it is assumed that before it diffuses into the solvent, some of AP4 accepts two more electrons from Zn to produce **6** and **7**. Based on the data that when TDM, with similar redoxive potential to Zn, is used as reducing agent the reaction gives only 1% AP4 it may be reasonable to assume that most of AP4 (if not all of it) was formed on the surface of Zn. The unsuccessful traditional high dilution methodology and the fact that more reactive TFFC dichloride **8** gave a lower yield may indicate that intermediate **3** should be produced at some optimal rate. At a lower rate most of **3** may diffuse into solvent before it decays on the zinc surface, and lead largely to oligomer and polymer. When more reactive **8** is used, intermediate **3** is generated at a much higher rate. Thus, even at the zinc surface it forms more polymer due to the higher probability for the chemical intermediates **4** to encounter monomer **2** before it undergoes intramolecular cyclization. Even though the exact reason that Zn metal enhances the formation of AP4 on its surface is unclear, dissolved **4** may either be formed in syn-form or *trans* may decrease the activation energy for **4**-extended monomer to **4**-syn (Scheme 5).

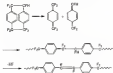


Scheme 9

3.1.3.1 Purification of AP4

The purification of AP4 is very important for its application in industry. Experiment as T can be first to the semiconductor application of AP4. If a mixture of AP4 and P is used to make the polymer film, the anthracenequinone monomer P will be produced, which will then be incorporated into the film. The produced film will thus have the moiety of CF₃COO, and at high temperatures this moiety is unstable and will eliminate

HF which will cause problems²². So the elimination of F as an impurity is essential for the industrial application of this new process.



Scheme 10

We first tried to purify the product by reprecipitation from benzene, but this was very inefficient and much HF was lost during the process, though the purity of 62% could be increased to 95 (57% based on OC analysis). A more efficient method was necessary to purify the product. The obvious way would be to convert F to 4-lyl elimination of HF under appropriate conditions and then get rid of 8. A lot of tests were carried and LiOH/THF²³ was found to be the best.

The conversion is 100% based on OC analysis, F disappeared completely after the reaction mixture was allowed to stir at r.t. for 30 minutes.



The conversion of 7 to 8 allowed us to focus on the removal of 6. The addition of Hg_2^{2+} to the double bond¹⁰ is one of the most used reactions in organic chemistry, and partially fluorinated alkenes react with Hg_2^{2+} readily under UV irradiation. It was found that the reaction of AP4 and 6 occurred with Hg_2^{2+} in 10 min at r.t. in chloroform with 100% conversion.

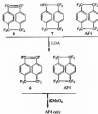


100

The staroformery is not identified, but since only one cancer was detected, we assumed that the immunohistochemical pattern was the only marker found. Unfortunately, the *diagnostic #8* could not be recovered from AJ4.

The isolation of **AP4** by the usual means is a self interest reaction in organic synthesis.²² It would be evident to the field **11**, **12** should be easily removed from **AP4** because of its totally different physical properties. It was found that treatment of the mixture of **6** and **AP4** in CH_2Cl_2 with an excess amount of KMnO_4 at room temperature overnight results the disappearance of **6** completely. Acetone and acetonitrile are also appropriate reaction solvents.

In conclusion, after the crude **AP4** is isolated, pure **AP4** (99.95%) can be obtained by two extra steps followed by recrystallization from benzene.



Scheme 13

After we finished the whole process, we found that the reaction of P_2 with double bonds was well studied²⁰ and if the reaction of P_2 with **4** was done and **2**₁ did not react with APH, we should be able to increase the total yield by about 10%. Luckily P_2 -did react with **4** at room temperature and did not require APH.



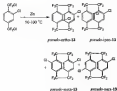
Scheme 14

Combining the ease of the new APH-forming and purification process with the fact that the dibkride **5** is much more readily prepared (a new and cheap process will be discussed in Chapter 7) than the dibkoxide, the current overall methodology for synthesis of APH should enable convenient, inexpensive and highly scalable preparation of APH for both research and commercial purposes.

1.2 Preparation of APH Derivatives

The successful preparation of APH provided us a very good opportunity to study the reactivity of APH with various reagents.²⁰⁻²² Since starting from TPPC dibkoxide, APH could be prepared in good yield under very mild reaction conditions,²⁰ it became interesting to see to what degree substitution on the ring of TPPC dibkoxide affected the new reaction and what the reactivity of such reagents might be.

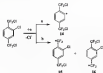
Heating a mixture of 1-chloro-1,4-bis(bromodifluoromethyl)benzene (2) obtained from **1** and two equivalents of *tert*-BuOK in DMSO at 90–100 °C for 16 h gave dibenzosilole **14** in 50% yield. Due to the rigid geometry of 1,1,2,2-tetrafluoroethane, the aromatic ring could not rotate through the parasilene axis, thus dibenzosilole **14** was obtained as *trans*-isomers, which could not be separated from one another by column chromatography. The lower yield may be caused by the steric effect of the bigger difluoro substituents compared to H, thus increasing the steric strain of the product, or perhaps enhanced reactivity to form the *cis*-isomerization of the dibenzosilole **4**.



Scheme 15

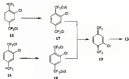
Even though two different chlorine substituents exist in the starting material (CF_2 -**2** and Ar -**2**), the two benzylic chlorines are apparently preferentially reduced, and

removed, probably due to the relative reluctance of an Ar-Cl bond to be cleaved at the radical reaction stage as an $\text{S}_{\text{N}}1$ process.



Scheme 10

Thus when Cl-TPFX dichloride accepted the first electron from the reducing agent Zn pathway b is predominant over path a for the elimination of $\text{Cl}^\bullet$ to form the radical intermediates. After the radicals 15 and 16 were formed, they were further reduced by Zn to give zinc reagent 17, 18 which completed the L_2H elimination to afford the key intermediate 2-chloro-2,5-bis(methylthio)benzophenone 19. Conversion of 19 gave the desired products.



Scheme 17

On the other hand, when the solvent was *n*-Bu, because *n*-Bu is better for the SET reaction, quite different results due to the weak C-Br bond. If the reaction was carried out at 50°C , only the reduced side product TTFX was detected after 50% conversion of 2-bromo-TTFX substrate **28**. However, when the reaction was carried out at 110°C , a mixture of AP4, monobromo-AP4 (**20**) and dibromo-AP4 (**22**) was detected (monobromo-AP4 + dibromo-AP4 = AP4 = 17%). This difference in reactivity can be ascribed to the different behavior of aryl bromide from aryl chloride in SET reaction. At lower temperature, single-electron-transfer mechanism appears to dominate, whereas at higher temperature two-electron transfer appears to be the major reaction pathway. To investigate the temperature dependence of the reaction, we assume that the 1,4-, two-electron elimination process has a greater temperature-dependence than the SET process.



Scheme 18

All the products were analysed by GC/MS. The isolation of the pure 20 and 21 was very difficult, as the relative ratio of 20 to 21 was not determined.

It is predicted that with more fluorine on the aromatic ring of AFI derivatives, the film generated from it will have lower dielectric constant. When 1-fluoro-2,3,5-trichlorobenzene (24) was allowed to react with 2Na in DMA solvent at 50 °C, after 3 hrs the reaction was finished and normal work-up gives difluoro-AFI (25) in 18% yield.



Scheme 19

When 1,2-difluoro-TTPX-dibromide (**26**) was used, tetrafluoro-AP4 (**26**, **27**) was obtained in only 9% yield. The reaction was carried out at 85 °C.



Scheme 20

Though both monofluoro-TTPX dibromide and difluoro-TTPX dibromide reacted with Zn in DMA to provide the expected AP4 derivatives, albeit at lower yields, when tetrafluoro-TTPX (**28**) was used, only the monomer (**28**) was detected.



Scheme 20

The monomer **29** was very stable in DMA solution, but trying to initiate a free DMA solution failed. Addition of bromine to the reaction mixture of **29** in DMA resulted the formation of the corresponding dibromide **30** in almost quantitative yield based on **29**. The reaction stopped immediately after the addition of Fe_2 .



Scheme 21

When 3-trifluoromethyl TFX dibromide (**31**) was used, a very complex reaction mixture was obtained, and no pure expected trifluoromethylated AP4 dimers were isolated.

2.1 Experimental Section

Starting material TPFX dihalide was prepared based on the reported method²⁷ from tetrakisopropylsilane. All the solvents were used as purchased without any other steps.

Typical procedure for the preparation of AP4 from TPFX dihalide: Into a 1 L three-necked round-bottomed flask are added 100 mL of *N,N*-dimethylacetamide (DMAc), *p*-tolaldehydefluoromethylfluorane (5) (50 g, 0.24 mol), and zinc dust (51 g, 0.96 mol). The mixture is heated over a period of 40 min to 100 °C under vigorous stirring and at 1% atmosphere, and it was quenched at that temperature for 4 h, after which no 5 remained and the solution had become yellow. The reaction mixture was then cooled to room temperature and filtered, washing the resulting oligomeric solids with two 10 mL portions of DMAc to extract small amounts of AP4. Combining these washings with the original DMAc filtrate, the impurities 4- and 6% yield) and hexafluoro[1,1]paracyclophane (7.1%) were removed by stirring the combined DMAc solution at room temperature with 5 g of K₂CO₃ overnight, followed by again filtering the mixture to obtain a clear colorless DMAc solution. The crude AP4 product was then obtained by evaporating the DMAc filtrate at 100 °C under full vacuum. After washing the resulting residue with water and cold methanol, the crude product was extracted with hexanes, the hexanes was evaporated, and the residue was recrystallized from hexane to give >99% pure AP4 (11.4 g, 40.1%). Pure 1,2,3,4,7,8,10-hexafluoro[1,1]paracyclophane-3-one (6) was obtained from the crude product by preparation GC: ¹H NMR(CDCl₃) δ 8.0

and δ (3) ($\Delta H_{\text{cal}} = 8.1 \text{ kJ}$) ^{19}F NMR (CDCl_3) δ 113.98 (s, 4F), -118.48 (s, 2F) IR (neat) ν_{max} for $\text{C}_{10}\text{H}_8\text{F}_6$ 144.833 cm^{-1} Calc. 314.0330

Typical procedure for the transformation of mixture of AP4 and 8: Into a 250 mL three-necked round-bottomed flask was added a mixture of AP4 (5) (containing AP4, 7 and 8) and 100 mL (dist. CH_2Cl_2 , P_2 in N_2 (95% in N_2) was then passed through anhydrous NaI packed column (to remove the remaining HF in P_2 gas), then the solution under vigorous stirring and heat through NaI solution. The reaction was carefully monitored by ^{19}F NMR, even though the appearance of light red color in NaI also suggests the reaction may be over. After the reaction was over, N_2 was allowed to flush the whole system for 30 min. Removal of the reaction solution and reprecipitation from hexane gave pure AP4 in over 90% yield.

Typical procedure for the transformation of 7 to 4: Into a 25 mL three-necked round-bottomed flask was added a mixture of crude AP4 (containing AP4, 7 and 8) and freshly distilled THF (10 mL). Under vigorous stirring, lithium diisopropylamide (3.1 mL, 1M in hexane) was added slowly at room temperature. ^{19}F analysis indicates the disappearance of 7 in 3 hrs. After the reaction was over, the reaction mixture was washed with HCl (1 x 10 mL) and brine (3 x 10) to neutral. The organic solution was dried over Na_2SO_4 . Evaporating the solvent gave the mixture of AP4 and 1 in 90% recovery.

Reaction of THF with TiCl_4 , dichloride: Into a 100 mL three-necked round-bottomed flask was added a mixture of TiCl_4 (60 mL) and TiF_3 dichloride (3 g). The

mixture was cooled to -45°C and TDAE (3.4 g) was added dropwise. After the addition of TDAE the reaction mixture was allowed to warm to room temperature (this was heated to 100°C under vigorous stirring). The reaction mixture became black and some white appeared. After the reaction was over, ^{13}C NMR showed the conversion of 4 was 100% and the ^{19}F NMR yield was 7% with 1,1,1,3,3,3-hexafluoro-2-propanol as internal standard.

Other reactions were carried out under similar procedures with appropriate catalyst and at desired reaction temperature.

Isomers 4F4: mixture of para-para, para-meta, para-ortho and para-meta-ortho- diisomers-1,1,1,3,3,3,3H-hexafluoro[1,1]paracyclophane was obtained when solid, ^{19}F NMR (CDCl_3) δ : -109.46—-118.38 (m) ppm. ^{13}C NMR: δ : 4.79 (s, 1 H), 4.99-7.31 (m, H_2 , 7.94 (s, 1 H), 7.71 (s, 2= 1.4 Hz), 6.10 (s, 1.75 (s, 1.94 (s, 1.79 (s, 6.76).

Isomers-4,1,1,1,3,3,3,3H-hexafluoro[1,1]paracyclophane m.p. $152-153^{\circ}\text{C}$. Four isomers were observed based on ^{19}F NMR analysis, the ratio is 1:33:6:65 or 34:6:58. ^{19}F NMR (acetone- d_6) δ : -103.66 (s, 1.33 F), -108.87 (m, 6.63 F), -105.41 (s, 2= 12.14 Hz F), -107.37 (s, 3.28 F), -110.56 = -115.48 (m, 14.33 F) ppm. ^{13}C NMR δ : 4.79 (s, 1= 10.30 Hz, 10 (s, 4 Hz, 2= 10.8 Hz, 1= 40 F), 7.33 (s, 2= 5.90 Hz, 1= 40 Hz, 7.36 (s, 2= 6.4 Hz, 1.74 Hz), 7.46 (s, 2= 6.4 Hz, 2.12 Hz, 7.58-7.63 (m, 2.12 Hz), 7.79 (s, 6.1 Hz, 1.49 (s) ppm. HRMS: Calc. for $\text{C}_{14}\text{H}_6\text{F}_6$ 344.0335, Found 344.0335.

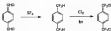
1,1,1,1,7,8,9,10,11,12,13,14-dodecafluoro[1,1]spirocyclopentane mp 54-55 °C. ^{19}F NMR(CDCl_3): δ -111 (m, 2F), -113 (m, 2F), δ -148 (s, 2F), 19 (s, 2F), -115 (m, 2F), -141 (s, 2F), 14 (s, 2F). ^1H NMR(CDCl_3): δ 7.12 (s, 1H), 6.1 (s, 1H). IR (KBr) cm^{-1} : 1656. Caled for $\text{C}_{10}\text{F}_{12}\text{H}_2$: 424.0421, Found: 424.0413.

Octafluorocyclopentane (28)-and- α,α' -difluorooctadecafluorocyclopentane (29) 28 (as DMA solution) ^{19}F NMR (CDCl_3): δ -450 (qF), -145 (qF). Into a solution (1 mL) of 28 in DMA was added bromine (0.1 mL) at room temperature. The reaction was over immediately after the addition of Br $_2$ based on ^{19}F NMR (CDCl_3): δ -45 (qF), -155 (qF) ppm.

CHAPTER 1 SYNTHESIS OF 1,4-DICHLORODIFLUOROBENZENE

1.1 Introduction

In the previous chapter we discussed the new method for synthesizing APF and its derivatives, with the key precursor for this process being bis-*p*-(chlorodifluoromethyl)benzene and its derivatives. To make the process more attractive for commercial application, an inexpensive method for making the dichlorodifluorobenzene derivative is desirable. Previously there was only one method reported for its synthesis. In the 1970s, Chow et al.¹⁰ reported that treatment of tetrachlorobenzene (**1**) with SF_6 (**2**) followed by the radical chlorination gave 1,4-dichloro-*p*-difluorobenzene (DDFC) derivative, **3** (Scheme 1).



Scheme 1

The major drawback for this process is the use of the expensive starting materials fluorinating reagent SF_6 in the first step.¹⁰

Later in our lab it was found that starting from 1,4-dichloro-*p*-difluorobenzene,

TBPA (4) can be obtained in high-yield by using CaH as the fluorinating reagent (Scheme 2).⁴⁰



Scheme 2

The use of expensive CaH and difficulties at scale-up will probably prevent this method from being used in industry.

Obviously a cost-effective method to prepare TTP & derivatives is essential for the commercialization of NPs, and in this chapter our new approach to synthesis of TTPS-derivatives will be discussed.

3.2 Results and Discussion

Chloro-fluor exchange reactions⁴¹ are some of the most frequently used reactions for preparing fluorine-containing compounds. Polydimethyl H² is the cheapest industrial source of fluorine for preparing fluorinated materials in such a manner. For example, the first fluorinated organic compound, trifluoromethyl isocyanide (H_3^{F}), was first prepared through the CHF exchange reaction:



Scheme 3

Since chlorinated compounds can be easily synthesized at a very low price, if a chlorinated precursor could be used in an HF reaction, the cost of TFX could decrease dramatically. Unfortunately, when α , α , α' , α' -tetrachloro- p -ylene was used in the presence of no-fluorinated product, TFX, was obtained, the reaction giving only polymers. Most stable²²



Scheme 4

Recent research²² disclosed an alternate method of synthesizing TFX in which α , α , α' , α' -tetrachloro- p -ylene (4) reacts with HF to produce TFX. The method employs the well established electrophilic catalyzed S_N1 reaction mechanism for replacement of halogenic halogen atoms of the TFX with fluorine atoms. According to this method, the primary source of HF acts as an electrophile which removes halogen from TFX to form a carbocation. The carbocation subsequently reacts with fluoride to form TFX after sequential S_N1 replacement. While the reaction is reported to provide a good yield when carried out under comparatively mild reaction conditions, safety-

containing compounds are highly toxic and expensive. Furthermore, the SOCl_2 is used in a stoichiometric rather than a catalytic amount, resulting in large quantities of hazardous waste materials. Therefore, this method of synthesizing TPPS has limited use for industrial applications.

m , n , n' , n'' , n''' -Fluorobenzene- p -toluene has been used in the industry to prepare 1,4-bis(trifluoromethyl)benzene.¹²



Scheme 3

The question was whether one could modify these reaction conditions so that the two CH_3 groups could be selectively transformed to CF_3 groups? A first attempt was run at $60\text{ }^\circ\text{C}$ without any solvent, and after 2 hrs a reaction mixture was obtained, no solid was formed during the reaction, but the major product was 1,4-bis(trifluoromethyl)benzene, with only a small amount of TPPS dichloride being detected after careful analysis. Upon further modification it was found that TPPS-dichloride could be obtained in more than 80% yield, with the major side products being under-fluorinated compounds (which can be re-used in the next run). A simple distillation gave TPPS-dichloride as 70% pure which is pure enough for the APF systems.



Scheme 4

The reaction temperature is very important for the reaction as presented in reasonable rate with high selectivity. At higher temperature the over-fluorinated products become predominant, whereas at lower temperature the reaction proceeds very slowly and the major products are under-fluorinated compounds. The addition of an inert organic solvent is also very important. When the reaction is carried out without solvent, the over-fluorinated products dominate.

Though the reaction can be carried out without catalyst, the addition of SnCl_4 as catalyst increases the rate and thus decreases the reaction time. In the presence of catalyst SnCl_4 , the reaction occurs at room temperature.

The Cl-N exchange reaction can also be applied to synthesize the other TFEH-substances, which were then used as the precursors of NFH derivatives. For example, starting from 3-fluoro-1,4-bis(methylcarbamoyl)benzene, 3-fluoro-1,4-bis(dichloromethylcarbamoyl)benzene can be prepared in 70% yield, because of the electron-withdrawing effect of the fluorine substance, the reaction temperature needs to be higher ($55\text{--}65\text{ }^\circ\text{C}$). The reaction can be carried out in the presence of *N*-butylmorpholine and in the absence of catalyst (Scheme 5).



Scheme 7

A small amount of over-fluorinated product, 2-fluoro-4-chlorobenzene, was detected (the chemical shift for CF_3 is -63.2 ppm, and it appears as a doublet with the $J_{\text{H-F}} = 5 \pm 1$ Hz).

When 1,4-dimethoxybenzene is used, the reaction is carried out at 30°C and the product can be obtained in 41% yield at 40 gram scale. The use of an excess amount of TiF_4 does not affect the yield (Scheme 8).



Scheme 8

3.3 Possible reaction mechanism

$\text{TiCl}_4/\text{CH}_2\text{Cl}_2$ exchange reaction with BF_3 is reported to go through a nucleophilic intermediate.²¹ Our results show that the electron withdrawing substituents on the ring deactivate the substrates, with the order of reactivity of the substrates being



This result is consistent with the stability of the carbenium. The other evidence that the reaction goes through the carbenium is that the presence of AlCl_3 increases the reaction rate and lowers the required reaction temperature from 41 °C to 31 °C. Apparently, the presence of two electron-withdrawing groups helps the reaction occur with high selectivity. When anisole/methyl benzoate was treated with H^+ even at 0 °C, only anisole/methyl benzoate was obtained. No *ortho*-methoxy/methyl benzoate was detected (Scheme 5).



Scheme 5

The general trend that increasing the number of fluorines on the carbon strengthens the other bonds in the same carbon²⁸ may also play an important role in the selectivity of the reactions.



In conclusion, TFE-dichloride can be synthesized by reacting bromodifluoropropane and HF. The reaction is carried out using a relatively small amount of an inert solvent. A preferred solvent is 1,2-dichloroethane. The reaction is of particular interest because high yields of TFE-dichloride can be obtained in a one-step process using readily available and inexpensive starting materials. The reaction is highly specific for forming the desired TFE-dichloride under mild conditions. The reaction has been observed to progress to a desired level of exchange between chlorine and fluorine constituents and then stop. In addition to the simplicity of the reaction, it is environmentally advantageous because it allows the solvent to be recycled, and it requires only slightly more than the stoichiometric amount of HF. Furthermore, any over-fluorinated byproducts of the reaction are valuable and in demand, and any under-fluorinated byproducts may be recycled. As such, the reaction generates very little waste.

3.4 Experimental Section

Typical procedure for preparation of TFX-dibutide: 350 g (1.1 mol) of hexachlorocyclene (HCCl₆) was placed into a 400 ml autoclave. 100 ml of 1,2-dichloroethane (DCE) and 200 g (1.5 mol) ethylenic HF were added. The mixture was stirred at room temperature for about 10 hours, during which time the pressure rose to approximately 3 atmospheres. Upon completion of the reaction, residual HF and HCl were removed by venting into 100 ml of 10% NaOH. The residual organic phase was then washed three times with 100 ml of 1% NaOH and then three times with 100 ml water. Subsequently, the organic phase was dried over MgSO₄. Simple distillation gave three fractions.

Fraction 1 (71-80 °C/15 mmHg) yielded 21.5 g of material comprising approximately 45% TFX-dibutide. Of the remaining material, a major portion comprised a perfluorocyclohex-ene product.

Fraction 2 (86-98 °C/10 mmHg) yielded 17 g of product comprised of approximately 45% TFX-dibutide.

Fraction 3 (95-107 °C/10 mmHg) yielded 27 g product comprising approximately 45% TFX-dibutide. Among the remaining 15% by-product, the major component was undifferentiated material.

The total yield of TFX-dibutide from the above reaction was about 75-85%.

The reaction of 2-fluoro-1,4-bis(methylsulfonyl)benzene with BF_3 was carried out under similar reaction conditions except that the temperature was 50–55 °C.

2-Fluoro-1,4-bis(methylsulfonyl)benzene (b.p. 110 °C/24 mmHg)
 (74.2%) ^{19}F NMR (CDCl_3) δ -30.60 (d, $J = 14.1$ Hz, 2F), 31.60 (s, 2F), -436.18 (m, 1F) ppm, ^1H NMR (CDCl_3) δ 7.48 (m, $J = 11.4$ Hz, 2H), 7.70 (s, $J = 11.4$ Hz, 2H) ppm.

1,4-Bis(methylsulfonyl)-1,4-bis(methylsulfonyl)benzene (81%) b.p. 120.2–124 °C/20 mmHg, ^{19}F NMR (CDCl_3) δ -31.43 (d, $J = 4.33$ Hz, 4F), -117.29 (m, 2F) ppm, ^1H NMR (CDCl_3) δ 7.48 (s, $J = 7.11$ Hz, 2H) Calc. for $\text{C}_{10}\text{H}_{12}\text{S}_4$ ^{19}F 281.9428 Found 281.9447

1,4-Bis(methylsulfonyl)-1,4-bis(methylsulfonyl)benzene (94%) colorless liquid, b.p. 113–115 °C/20 mmHg, ^{19}F NMR (CDCl_3) δ -47.61 (s, $J = 4.88$ Hz, 4F), -136.15 (t, $J = 4.44$ Hz, 4F) ppm. Calc. for $\text{C}_{10}\text{H}_{12}\text{S}_4$ ^{19}F 281.9348 Found 281.9342

CHAPTER 4 ELECTROPHILIC SUBSTITUTION OF 1,2,3,4-*trans*- OCTAFLUORO-1,3-DIAZACYCLOPHANE

4.1 Introduction

The synthesis of AF-4 (**1**) and some of its derivatives was achieved starting from the TFPX-dichloride (**2**)¹⁸ and its derivatives. The limitation of this ring methodology becomes obvious when the substitution on the aromatic ring of the TFPX-dichloride increases. Though AF-4 was prepared from TFPX-dichloride in good yield (40-45%), when the TFPX-dichloride derivatives, such as 2-chloro- (**3**), 2-bromo- (**4**) were used, the corresponding AF-4 derivatives were obtained in only 10-15% yields, and 2-iodo-TFPX-dichloride (**5**) gave only a mixture of AF-4, bromo-AF4 (**6**) and iodo-AF4 (**8**). When Cl-TPFX-dichloride (**3**) was used only isopropylated product was obtained although triisopropylammonium AF-4 anions (**7**) were detected from GC/MS.

With the availability of AF-4 further functionalization of AF-4 could provide an alternative useful method to prepare AF-4 derivatives.

Although organic chemistry has been limited to a wide variety of aromatic [1,3]paracyclophane (**1**)¹⁹⁻²² chemistry over the years, fluorinated cyclophane chemistry has received much less attention, and paracyclophane bearing more than a couple of fluorine atoms are very scarce in the literature.

A detailed investigation into the chemistry of AP4 has been hampered by the lack of a viable large-scale synthesis of the desired compound²⁷⁻²⁸. Until the investigation on the reactivity of AP4 in our lab, only one ring-substituted derivative of 1,1',3,3'-bis(4,6-dimethyl-2-pyridyl)-4,4'-biphenyl was reported in the literature²⁹, and the procedure proved not to be reproducible.

4.2 Results and Discussion

4.2.1 Electrophilic Substitution of AP4

Organic halides are among the most valuable compounds in organic synthesis and electrophilic halogenation of arenes is one of the most popular used reactions in organic chemistry. It was pointed²⁹ that reaction of AP4 with Br_2 in the presence of Fe catalyst resulted the pseudo-pure-dibromo-AP4 (BT).

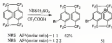


Scheme 1

Unfortunately, when we repeated the reaction under various reaction conditions, no reaction was detected (with only the starting material being recovered after work-up).

It was proposed that AP4 itself is a good electron donor, behaves like a deactivated aromatic system because of the fluoromethyl substituents³⁰ and it is therefore not reacting with AP4 as the reaction to the electrophilic substitution.

bromination of disubstituted aromatic compounds such as naphthalene was reported in the literature by using $\text{NBS}/\text{H}_2\text{SO}_4$ system²⁷⁻²⁹. When such brominating conditions were applied to A^{H} , no reaction was observed, and only the starting material being recovered. When NBS was mixed with H_2SO_4 , a solid complex was formed, A^{H} could not react with the solubilized brominating agent. Upon slight modification of the reaction by adding trifluoroacetic acid as reaction solvent, the bromination occurred smoothly, and depending on different ratio of NBS to A^{H} , monobromo- A^{H} or dibromo- A^{H} could be obtained (Scheme 2).



Scheme 2

Different from the early patent's claim, the major product from dibromination of A^{H} was *p*-dibromo- A^{H} instead of pseudo-*para*-isomer!

Trifluoroacetic acid proved to be critical to the reaction. When halobenzoic solvents, such CCl_4 or CH_2Cl_2 were used, no reaction occurred. When other inorganic acids such as H_3PO_4 were used instead of TFA, though the brominating agent dissolved completely, no bromination was detected. The failure of the reaction was probably due to the unavailability of the A^{H} or inorganic acids. When acetic acid was used instead of TFA, bromination of the α -trifluoromethyl acid was observed to occur prior to the bromination of A^{H} (Scheme 3)³⁰.



Scheme 2

The separation of the monomeric API from API is very simple, as API is a highly symmetric molecule, its solubility in toluene is much lower than that of the asymmetric molecule, trans-API. By simple recrystallization from toluene, trans-API could be obtained from another toluene or CH₂Cl₂ purity along with 100% API.

To extend the application of this new powerful brominating reagent, other deactivated aromatic compounds were also tested (Scheme 3).



Scheme 3

Table 1. Reactions of aromatic compounds with NBS/TTA-H₂SO₄.

Substrate	NBS/TTA (mol)	T (h)	Yield%	Sp (C) (h)
m-Cl-C ₆ H ₄ -CH ₃	0.4	30	84	12, 13, 14, 15, 16 ^a
p-Cl-C ₆ H ₄ -CH ₃	0.1	36	62	17, 18, 19, 20 ^a
p-Cl-C ₆ H ₄ -CH ₂ CH ₃	0.2	64	84	21, 22, 23, 24, 25, 26 ^a
m-Cl-C ₆ H ₄ -CH ₂ CH ₃	0.4	36	45	27, 28, 29, 30, 31, 32 ^a
C ₆ H ₅ -CH ₃	0.3	36	81	33, 34, 35, 36 ^a
C ₆ H ₅ -NO ₂	0.1	24	88	37, 38, 39, 40 ^a
C ₆ H ₅ -COOH	0.2	36	76	41, 42, 43, 44 ^a
C ₆ H ₅ -CHO	0.1	32	84	45, 46, 47, 48, 49, 50 ^a
C ₆ H ₅	0.1	2	91	51, 52, 53, 54 ^a

4.1.1 Synthesis of Naph-P4 and its Transformation

Synthesis of AP4 has been recently reported from this lab²⁰, but the actual preparation had to be carried out under relatively harsh conditions. Over a period of 24 h, concentrated (90%) nitric acid at 100 °C, whether neat, with concentrated sulfuric acid, or in sulfonic, generating numerous derivatives AP4 in moderate yield (20-40%). The sparsity of the reaction conditions and only moderate yield of the product reflect the low reactivity of this fluorinated ester with respect to electrophilic substitution. The best isolated yield (30%) of AP4 was obtained when expensive potassium persulfate/sulfuric acid was used as the oxidizing agent.²⁰ It was, of course, found that AP4 could be used as a valuable starting material for preparing other AP's derivatives. It would therefore be desirable to develop an efficient method to produce AP4 under reaction conditions with cheap starting materials, instead of expensive persulfate/sulfuric acid.

Fortunately, it was found that by simply increasing the concentration of nitric acid, AP4 could be easily prepared in high yield under very mild reaction conditions. When AP3 was allowed to react with fuming nitric acid (70%) at room temperature, after 5-10 hrs a homogeneous solution was produced.²⁰ NMR showed the reaction to be complete. After work-up, a white solid was obtained and the yield was virtually quantitative. No further purification was needed for the further transformation.



Scheme 5

Attempt to add the second nitro group failed using fuming HNO_3 . When the reaction was carried out at elevated temperature, $50\text{--}60^\circ\text{C}$, the reaction just gave complex mixture. The nitro group addition and male decomposition goes on, with no pure dinitro *APV* being able to be isolated.

The reduction of **28** was carried out in ethanol solvent. Drawing from the previous method²⁴ azobisisobutyronitrile was found to enhance the solubility of **28** thus making the reduction much easier (Scheme 6).



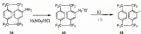
Scheme 6

The monofluorinated (2,6)pyridinediylfluoride anion is reported to be prone to nucleophilic decomposition,²⁵ whereas **29** is very stable. This difference can be attributed to

the inductive influence of the bridge fluorines, which should make **29** negatively less prone to oxidation.

Compound **29** proved to be an excellent precursor of a variety of other monosubstituted derivatives of Γ^{2+20} . Examining the disubstitution-and Sandmeyer-type chemistry of **29**, a number of other derivatives including halo-, trifluoromethyl-, and AP4-derivatives, etc. were produced in good yields. The problem of low solubility of **29** in the aqueous strong acid used for the Sandmeyer reactions could be overcome by the use of some acid as solvent.

In preparing the diazonium salt in acetic acid solvent at 0-1 °C, **29** did not dissolve at first, when all the solid finally dissolved, a brown solution was formed, and the reaction mixture was further stirred for 20 min at 0 °C. The mixture was very colorless in the solution of NaNO_2 , needed to be added slowly to keep the temperature under 1 °C. Once the diazonium salt was formed, the solution was poured into a solution of KI under vigorous stirring, and the pure white AP4 was obtained in high yield (Scheme 7).



Scheme 7

The apolo formation is especially important synthetically, because of its reaction versatility. Different from the parent compound AP4, **44** can dissolve in most organic solvents very easily at room temperature.

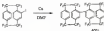
It is well documented that when the copolymerase was treated with Cu in polar solvent such as DMF, the Ullmann coupling reaction will afford the dimer products (Scheme 3).²⁰



Scheme 3

Heating the reaction mixture of poly-4, copper powder and DMF at 110–140 °C for 5 hrs gave the AP4 dimer (**4B**) at 40% yield with AP4 as the only side product.

Scheme 4:

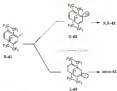


Scheme 4

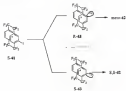
A high concentration of **4B** is essential for the success of the coupling reaction. With diluted poly-AP4, only reduced product was obtained. On the other hand, in the presence of Pd catalyst²¹, the reaction can be carried out at lower concentration with higher yield. When bromo-4B was used instead of poly-AP4, no coupling product was observed, only the reduced product, AP4 was obtained from the reaction mixture.²²

Due to the steric effect the copolymer may cannot couple freely through the para-phenylene unit at ordinary temperature. Therefore **4B** was actually produced as a pair of terminally monosubstituted monomers: 5-**4B** and 6-**4B**. Therefore when **4B** reacted with

copper powder, two enantiomeric copper(II) salts were formed: **5-43** and **5-45**. These two copper salts reacted with **5-44** and **5-46** resulted three diastereic compounds: **nano-42** and **dl-42**. The dl isomers can be separated by column chromatography. Single crystals were obtained for both **nano-42** and **dl-42** and X-ray crystal structure analyses were obtained (Scheme 10).



Scheme 18 (continued)



Scheme 19

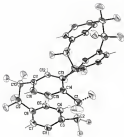


Figure 1 X-ray crystal structure of **42**

Table 2. Crystal data and structure refinement for **10b**.

Empirical formula	C ₂₁ H ₁₈ Fe	
Formula weight	266.23	
Temperature	175(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C ₂	
Unit cell dimensions	<i>a</i> = 7.356(5) Å	<i>α</i> = 90°
	<i>b</i> = 21.347(5) Å	<i>β</i> = 109.44(2)°
	<i>c</i> = 17.933(3) Å	<i>γ</i> = 90°
Volume	2628.1(7) Å ³	
Z	4	
Density (calculated)	1.7610 g/cm ³	
Absorption coefficient	0.482 mm ⁻¹	
F(000)	1408	
Crystal size	0.073 × 0.12 × 0.40 mm ³	
Data range for data collection	1.00 to 25.00°	
Index ranges	-0.9 < <i>h</i> < 9, -0.02 < <i>k</i> < 0.02, -10 < <i>l</i> < 12	
Reflections collected	18812	
Independent reflections	5529 [<i>R</i> _{int}] = 0.0475	
Completeness data = 25.00°	98.3 %	
Absorption correction	Empirical	
Max. and min. transmission	0.996 and 0.146	
Reflections merged	Full matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	18811 / 2 / 163	
Goodness-of-fit on <i>F</i> ²	1.056	
Final <i>R</i> index [<i>R</i> - <i>R</i> _{int}]	0.1 = 0.1550, <i>wR</i> = 0.0553 (obs.)	
<i>R</i> index (all data)	0.1 = 0.1600, <i>wR</i> = 0.0609	
Absolute structure parameter	0.003	
Extinction coefficient	0.0001(2)	
Largest diff. peak and hole	0.174 and -0.178 e/Å ³	

$$R_1 = \sum |F_o| - |F_c| / \sum |F_o|$$

$$wR_2 = \left(\sum w(F_o - F_c)^2 / \sum w(F_o)^2 \right)^{1/2}$$

$$R = \left(\sum |F_o|^2 - 2 \sum |F_o| |F_c| + \sum |F_c|^2 \right)^{1/2} / \left(\sum |F_o|^2 + \sum |F_c|^2 \right)^{1/2} \quad \text{for } w = 1 / (\sigma(F_o)^2 + (\sigma(F_c))^2)$$

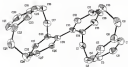


Figure 3. ORTEP structure of **6b** (H and F atoms are omitted).

Table 3: Crystal film and structure refinements for 4b-4d

Identification code	4b-1	
Empirical formula	C ₂₂ H ₁₈ F ₁₀	
Formula weight	460.47	
Temperature	170(2)K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /a	
Unit-cell dimensions	$a = 11.158(5)$ Å	$\mu = 0.07$
	$b = 12.408(8)$ Å	$\rho = 1.44$ g/cm ³
	$c = 11.158(5)$ Å	$\nu = 0.07$
Volume	1541.4(19) Å ³	
Z	8	
Density (calculated)	1.391 Mg/m ³	
Absorption coefficient	0.340 mm ⁻¹	
F(000)	2000	
Crystal size	0.08 x 0.10 x 0.15 mm ³	
Theta range for data collection	2.12 to 25.00°	
Index ranges	-10<h>10, -10<k>10, -11<l>11	
Difference in formal	0.024	
Independent reflections	1034 [R _{int} = 0.0023]	
Completeness in data = 100%	100.0 %	
Absorption correction	Integration	
Max. and min. transmission	0.9978 and 0.9951	
Difference method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1038 / 0 / 130	
Goodness-of-fit on F ²	1.000	
Final R ₁ index [I>2sigma(I)]	R ₁ = 0.0400, wR ₂ = 0.1400 [mu(I)]	
R ₂ index [all data]	R ₂ = 0.1000, wR ₂ = 0.1400	
Extinction coefficient	0.000(5) Å ⁻¹	
Largest diff. peak and hole	0.087 and 0.044 e Å ⁻³	

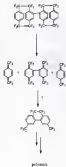
$$R_1 = \sum |F_o - F_c| / \sum F_o$$

$$wR_2 = \left(\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4 + 2F_o^2F_c^2 + F_c^4) \right)^{1/2}$$

$$R = \sum |F_o - F_c| / \sum |F_o| \quad \text{and} \quad wR_2 = \left(\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4 + 2F_o^2F_c^2 + F_c^4) \right)^{1/2} \quad \mu = 1.44 \text{ g/cm}^3 \quad \rho = 1.39 \text{ g/cm}^3$$

From the parameters of X-ray crystal structure, it can be seen that the bond length between the C-C bond joining the two AF4 molecules is shorter than normal C-C σ bond (1.35 Å vs 1.54 Å and 1.35 Å for toluene²⁰). While the free radical produced dimer have longer C-C σ bond (1.38 Å). This strong bond was also verified by the mass spectrum (M2). For the free radical dimer the standard peak is 54 kDa while the dimer gave the standard peak is 66. Different from the free radical dimer, the dimer did not decompose even at 150 °C.

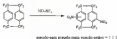
With the strong joint C-C σ bond, it would be possible to use it as a CVD precursor to draw films that may have different properties (Scheme 1).



Scheme 11

4.3 Synthesis of Desubstituted AP4

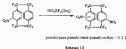
Though the monosubstituted AP4 derivatives were synthesized starting from the mono-AP4, the use of fuming nitric acid did not affect the desubstituted AP4. It was reported that in the presence of excess amount of $\text{HNO}_3/\text{H}_2\text{SO}_4$, desubstituted AP4 was obtained in good yield starting from AP4.⁴⁰



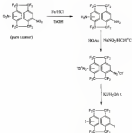
Scheme 12

The disadvantage for this reaction is that, much excess of expensive reagents (nitrosophosphoric acid) is to be used in order to obtain high yield. The improved method of using fuming nitric acid gave mono-AP4 in over 80% yield. Therefore to make the di-subst-AP4 cheaper, the best way may be starting from the mono-subst-AP4.

Treatment of monosubst-AP4 with 2 equiv. of nitric acid/sulfuric acid at 80 °C resulted in formation of the desired di-subst-AP4 in good yield, with the same regioselectivity as observed in the reported procedure.



The three isomers were separated by the reported method,²⁷ and after refluxing by FeCl_3 , the mono-derivatives were obtained. Following the reported method with some modification, some diethylAP1-derivatives were then synthesized in good yield.



Scheme 14

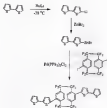
The solution of bis-dissociation salt is relatively stable, compared with the mono-dissociation salt, when the bis-dissociation salt solution was mixed with $\text{K}_2\text{S}_2\text{O}_8$; its decomposition is slower, and the dissoluble was obtained only after 12 hrs. Different from the previous report, the decomposition of the dissociation salt was allowed to proceed at room temperature.

Very recently Zhai²² et al reported that via the functionalization of [2,2]paracyclophane, the through-space charge transfer and nonlinear optical properties

could be studied. The authors claimed that such non-conjugated system with π - π interactions through space showed unique H₂O sorption. The polarity of the [2,2]phenylenephosphine derivative is bigger than the additive effect of the substituents.

Thiophene derivatives are very important precursors for the synthesis of conductive organic polymers.¹² In cooperation with the French-Chinese Marie Curie Unit, we synthesized the bis-thiophene A2N derivatives, and its oxidative polymerization gave the thiophene like polymers which showed moderate conductivity.

Treatment of bis-thiophene monomer 8 eq. allylaryl lithium in freshly distilled THF at -78 °C gave the mono-allylated bis-thiophene, and the resulting monomer mixture was treated with acetylene gas in same THF solution. The metal-exchange reaction afforded stable bis-triethynyl monomer. A Pd mediated coupling reaction at 60 °C gave the desired product in high yield.



Scheme 23

4.4 Experimental Section

4-Bromo-1,1,2,3,5,6,10,10-octabromo[1,2]germyclophane. A trifluoroacetic acid solution (20 mL) containing 1-(1,2,3,5,6,10,10-octabromo[1,2]germyclophane) (3.00 g, 3.7 mmol) and *N*-bromosuccinimide (3.9 g, 3.7 mmol) was stirred magnetically in a flask protected by a glass drying tube. After 3 min, 98% sulfuric acid (3 mL) was added, and left in situ for 14 h. After the same analysis by ^{75}P NMR and TLC showed the presence of starting material, mono-bromo AP4 and very small amount of some brominated products. The reaction was returned to 40 °C and left another 12 h. The mixture was cooled to ambient temperature, and added to 100 mL of ice-water. The precipitated product was filtered and washed with water to give 1.8 mmol of pure 4-bromo-1-(1,2,3,5,6,10,10-octabromo[1,2]germyclophane) (containing ca. 10% AP4) (2.1 g, 47%). ^1H NMR (CDCl_3) δ 6.9 (d, $^3J = 1.40$ Hz, 1H), 7.1 (t, q, 1H), 7.14 (s, 7.304 (s, 1H), ^{75}P NMR (CDCl_3) δ 113.28 (q, $^1J = 244.79$ Hz, $^{10}\text{P}_2$), 113.278 (s, $^1J = 244.79$ Hz, $^{10}\text{P}_1$), -119.275 (q, $^2J = 257.36$ Hz, $^{10}\text{P}_2$), -119.273 (q, $^2J = 257.36$ Hz, $^{10}\text{P}_1$), -114.904 (q, $^1J = 258.96$ Hz, $^{10}\text{P}_1$), -114.973 (q, $^1J = 259.90$ Hz, $^{10}\text{P}_2$), -114.795 (m, ^{20}P) MS m/z 422 (98%), 392 (24), 438 (2), 284 (2), 294 (2), 179 (100).

p-Bromo-1,1,1,1,3,3,5,5,10,10-octabromo[2,2]germyclophane. A trifluoroacetic acid solution (3 mL) containing 1-(1,1,1,1,3,3,5,5,10,10-octabromo[2,2]germyclophane) (3.00 g, 3.34 mmol) and *N*-bromosuccinimide (3.60 g, 11.20 mmol) was stirred magnetically in a flask protected by a glass drying tube. After 3 min, 98% sulfuric acid (3 mL) was added, and left in situ for 14 h. After the same analysis by ^{75}P NMR and TLC showed the presence of starting material, mono-bromo AP4 and

4-Amino-1,1,2,2,4,5,10,10-octahydro[1,2]quinoxaline-3,6-dicarboxylic-phthalic (H₂). A suspension of 4-amino-1,1,2,2,4,5,10,10-octahydro[1,2]quinoxaline-3,6-dicarboxylic-phthalic 38 (7.6 g, 10 mmol) in ethanol (50 mL) was stirred for 15 min at room temperature. Then powder (7.6 g, 10 mmol) was added, and the reaction mixture was heated to reflux. Concentrated hydrochloric acid (20 mL) was added dropwise to the mixture, and reflux was continued for 4 h. After this time, the mixture was cooled to room temperature and added to ice-water (200 mL). The solids then produced were filtered and redissolved in chloroform. This chloroform solution was filtered and evaporated, and the solid residue was chromatographed (dioxane/tetrahydrofuran 1/1) to give 48 (5.4 g, 60%) 4-amino-1,1,2,2,4,5,10,10-octahydro[1,2]quinoxaline-3,6-dicarboxylic-phthalic 48 (5.4 g, 60%) mp 223–225 °C. ¹H NMR (CDCl₃/d₂O 7:3) δ: ¹H = 4.18 (H_A, 1H), 4.23 (H_B, 1H), 4.24 (H_C, 1H), 4.25 (H_D, 1H), 4.26 (H_E, 1H), 4.27 (H_F, 1H), 4.28 (H_G, 1H), 4.29 (H_H, 1H), 4.30 (H_I, 1H), 4.31 (H_J, 1H), 4.32 (H_K, 1H), 4.33 (H_L, 1H), 4.34 (H_M, 1H), 4.35 (H_N, 1H), 4.36 (H_O, 1H), 4.37 (H_P, 1H), 4.38 (H_Q, 1H), 4.39 (H_R, 1H), 4.40 (H_S, 1H), 4.41 (H_T, 1H), 4.42 (H_U, 1H), 4.43 (H_V, 1H), 4.44 (H_W, 1H), 4.45 (H_X, 1H), 4.46 (H_Y, 1H), 4.47 (H_Z, 1H), 4.48 (H_{AA'}, 1H), 4.49 (H_{BB'}, 1H), 4.50 (H_{CC'}, 1H), 4.51 (H_{DD'}, 1H), 4.52 (H_{EE'}, 1H), 4.53 (H_{FF'}, 1H), 4.54 (H_{GG'}, 1H), 4.55 (H_{HH'}, 1H), 4.56 (H_{II'}, 1H), 4.57 (H_{JJ'}, 1H), 4.58 (H_{KK'}, 1H), 4.59 (H_{LL'}, 1H), 4.60 (H_{MM'}, 1H), 4.61 (H_{NN'}, 1H), 4.62 (H_{OO'}, 1H), 4.63 (H_{PP'}, 1H), 4.64 (H_{QQ'}, 1H), 4.65 (H_{RR'}, 1H), 4.66 (H_{SS'}, 1H), 4.67 (H_{TT'}, 1H), 4.68 (H_{UU'}, 1H), 4.69 (H_{VV'}, 1H), 4.70 (H_{WW'}, 1H), 4.71 (H_{XX'}, 1H), 4.72 (H_{YY'}, 1H), 4.73 (H_{ZZ'}, 1H), 4.74 (H_{AA''}, 1H), 4.75 (H_{BB''}, 1H), 4.76 (H_{CC''}, 1H), 4.77 (H_{DD''}, 1H), 4.78 (H_{EE''}, 1H), 4.79 (H_{FF''}, 1H), 4.80 (H_{GG''}, 1H), 4.81 (H_{HH''}, 1H), 4.82 (H_{II''}, 1H), 4.83 (H_{JJ''}, 1H), 4.84 (H_{KK''}, 1H), 4.85 (H_{LL''}, 1H), 4.86 (H_{MM''}, 1H), 4.87 (H_{NN''}, 1H), 4.88 (H_{OO''}, 1H), 4.89 (H_{PP''}, 1H), 4.90 (H_{QQ''}, 1H), 4.91 (H_{RR''}, 1H), 4.92 (H_{SS''}, 1H), 4.93 (H_{TT''}, 1H), 4.94 (H_{UU''}, 1H), 4.95 (H_{VV''}, 1H), 4.96 (H_{WW''}, 1H), 4.97 (H_{XX''}, 1H), 4.98 (H_{YY''}, 1H), 4.99 (H_{ZZ''}, 1H), 5.00 (H_{AA'''}, 1H), 5.01 (H_{BB'''}, 1H), 5.02 (H_{CC'''}, 1H), 5.03 (H_{DD'''}, 1H), 5.04 (H_{EE'''}, 1H), 5.05 (H_{FF'''}, 1H), 5.06 (H_{GG'''}, 1H), 5.07 (H_{HH'''}, 1H), 5.08 (H_{II'''}, 1H), 5.09 (H_{JJ'''}, 1H), 5.10 (H_{KK'''}, 1H), 5.11 (H_{LL'''}, 1H), 5.12 (H_{MM'''}, 1H), 5.13 (H_{NN'''}, 1H), 5.14 (H_{OO'''}, 1H), 5.15 (H_{PP'''}, 1H), 5.16 (H_{QQ'''}, 1H), 5.17 (H_{RR'''}, 1H), 5.18 (H_{SS'''}, 1H), 5.19 (H_{TT'''}, 1H), 5.20 (H_{UU'''}, 1H), 5.21 (H_{VV'''}, 1H), 5.22 (H_{WW'''}, 1H), 5.23 (H_{XX'''}, 1H), 5.24 (H_{YY'''}, 1H), 5.25 (H_{ZZ'''}, 1H), 5.26 (H_{AA''''}, 1H), 5.27 (H_{BB''''}, 1H), 5.28 (H_{CC''''}, 1H), 5.29 (H_{DD''''}, 1H), 5.30 (H_{EE''''}, 1H), 5.31 (H_{FF''''}, 1H), 5.32 (H_{GG''''}, 1H), 5.33 (H_{HH''''}, 1H), 5.34 (H_{II''''}, 1H), 5.35 (H_{JJ''''}, 1H), 5.36 (H_{KK''''}, 1H), 5.37 (H_{LL''''}, 1H), 5.38 (H_{MM''''}, 1H), 5.39 (H_{NN''''}, 1H), 5.40 (H_{OO''''}, 1H), 5.41 (H_{PP''''}, 1H), 5.42 (H_{QQ''''}, 1H), 5.43 (H_{RR''''}, 1H), 5.44 (H_{SS''''}, 1H), 5.45 (H_{TT''''}, 1H), 5.46 (H_{UU''''}, 1H), 5.47 (H_{VV''''}, 1H), 5.48 (H_{WW''''}, 1H), 5.49 (H_{XX''''}, 1H), 5.50 (H_{YY''''}, 1H), 5.51 (H_{ZZ''''}, 1H), 5.52 (H_{AA'''''}, 1H), 5.53 (H_{BB'''''}, 1H), 5.54 (H_{CC'''''}, 1H), 5.55 (H_{DD'''''}, 1H), 5.56 (H_{EE'''''}, 1H), 5.57 (H_{FF'''''}, 1H), 5.58 (H_{GG'''''}, 1H), 5.59 (H_{HH'''''}, 1H), 5.60 (H_{II'''''}, 1H), 5.61 (H_{JJ'''''}, 1H), 5.62 (H_{KK'''''}, 1H), 5.63 (H_{LL'''''}, 1H), 5.64 (H_{MM'''''}, 1H), 5.65 (H_{NN'''''}, 1H), 5.66 (H_{OO'''''}, 1H), 5.67 (H_{PP'''''}, 1H), 5.68 (H_{QQ'''''}, 1H), 5.69 (H_{RR'''''}, 1H), 5.70 (H_{SS'''''}, 1H), 5.71 (H_{TT'''''}, 1H), 5.72 (H_{UU'''''}, 1H), 5.73 (H_{VV'''''}, 1H), 5.74 (H_{WW'''''}, 1H), 5.75 (H_{XX'''''}, 1H), 5.76 (H_{YY'''''}, 1H), 5.77 (H_{ZZ'''''}, 1H), 5.78 (H_{AA''''''}, 1H), 5.79 (H_{BB''''''}, 1H), 5.80 (H_{CC''''''}, 1H), 5.81 (H_{DD''''''}, 1H), 5.82 (H_{EE''''''}, 1H), 5.83 (H_{FF''''''}, 1H), 5.84 (H_{GG''''''}, 1H), 5.85 (H_{HH''''''}, 1H), 5.86 (H_{II''''''}, 1H), 5.87 (H_{JJ''''''}, 1H), 5.88 (H_{KK''''''}, 1H), 5.89 (H_{LL''''''}, 1H), 5.90 (H_{MM''''''}, 1H), 5.91 (H_{NN''''''}, 1H), 5.92 (H_{OO''''''}, 1H), 5.93 (H_{PP''''''}, 1H), 5.94 (H_{QQ''''''}, 1H), 5.95 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(H_{UU''''''''''''''''}, 1H), 8.59 (H_{VV''''''''''''''''}, 1H), 8.60 (H_{WW''''''''''''''''}, 1H), 8.61 (H_{XX''''''''''''''''}, 1H), 8.62 (H_{YY''''''''''''''''}, 1H), 8.63 (H_{ZZ''''''''''''''''}, 1H), 8.64 (H_{AA'''''''''''''''''}, 1H), 8.65 (H_{BB'''''''''''''''''}, 1H), 8.66 (H_{CC'''''''''''''''''}, 1H), 8.67 (H_{DD'''''''''''''''''}, 1H), 8.68 (H_{EE'''''''''''''''''}, 1H), 8.69 (H_{FF'''''''''''''''''}, 1H), 8.70 (H_{GG'''''''''''''''''}, 1H), 8.71 (H_{HH'''''''''''''''''}, 1H), 8.72 (H_{II'''''''''''''''''}, 1H), 8.73 (H_{JJ'''''''''''''''''}, 1H), 8.74 (H_{KK'''''''''''''''''}, 1H), 8.75 (H_{LL'''''''''''''''''}, 1H), 8.76 (H_{MM'''''''''''''''''}, 1H), 8.77 (H_{NN'''''''''''''''''}, 1H), 8.78 (H_{OO'''''''''''''''''}, 1H), 8.79 (H_{PP'''''''''''''''''}, 1H), 8.80 (H_{QQ'''''''''''''''''}, 1H), 8.81 (H_{RR'''''''''''''''''}, 1H), 8.82 (H_{SS'''''''''''''''''}, 1H), 8.83 (H_{TT'''''''''''''''''}, 1H), 8.84 (H_{UU'''''''''''''''''}, 1H), 8.85 (H_{VV'''''''''''''''''}, 1H), 8.86 (H_{WW'''''''''''''''''}, 1H), 8.87 (H_{XX'''''''''''''''''}, 1H), 8.88 (H_{YY'''''''''''''''''}, 1H), 8.89 (H_{ZZ'''''''''''''''''}, 1H), 8.90 (H_{AA''''''''''''''''''}, 1H), 8.91 (H_{BB''''''''''''''''''}, 1H), 8.92 (H_{CC''''''''''''''''''}, 1H), 8.93 (H_{DD''''''''''''''''''}, 1H), 8.94 (H_{EE''''''''''''''''''}, 1H), 8.95 (H_{FF''''''''''''''''''}, 1H), 8.96 (H_{GG''''''''''''''''''}, 1H), 8.97 (H_{HH''''''''''''''''''}, 1H), 8.98 (H_{II''''''''''''''''''}, 1H), 8.99 (H_{JJ''''''''''''''''''}, 1H), 9.00 (H_{KK''''''''''''''''''}, 1H), 9.01 (H_{LL''''''''''''''''''}, 1H), 9.02 (H_{MM''''''''''''''''''}, 1H), 9.03 (H_{NN''''''''''''''''''}, 1H), 9.04 (H_{OO''''''''''''''''''}, 1H), 9.05 (H_{PP''''''''''''''''''}, 1H), 9.06 (H_{QQ''''''''''''''''''}, 1H), 9.07 (H_{RR''''''''''''''''''}, 1H), 9.08 (H_{SS''''''''''''''''''}, 1H), 9.09 (H_{TT''''''''''''''''''}, 1H), 9.10 (H_{UU''''''''''''''''''}, 1H), 9.11 (H_{VV''''''''''''''''''}, 1H), 9.12 (H_{WW''''''''''''''''''}, 1H), 9.13 (H_{XX''''''''''''''''''}, 1H), 9.14 (H_{YY''''''''''''''''''}, 1H), 9.15 (H_{ZZ''''''''''''''''''}, 1H), 9.16 (H_{AA'''''''''''''''''''}, 1H), 9.17 (H_{BB'''''''''''''''''''}, 1H), 9.18 (H_{CC'''''''''''''''''''}, 1H), 9.19 (H_{DD'''''''''''''''''''}, 1H), 9.20 (H_{EE'''''''''''''''''''}, 1H), 9.21 (H_{FF'''''''''''''''''''}, 1H), 9.22 (H_{GG'''''''''''''''''''}, 1H), 9.23 (H_{HH'''''''''''''''''''}, 1H), 9.24 (H_{II'''''''''''''''''''}, 1H), 9.25 (H_{JJ'''''''''''''''''''}, 1H), 9.26 (H_{KK'''''''''''''''''''}, 1H), 9.27 (H_{LL'''''''''''''''''''}, 1H), 9.28 (H_{MM'''''''''''''''''''}, 1H), 9.29 (H_{NN'''''''''''''''''''}, 1H), 9.30 (H_{OO'''''''''''''''''''}, 1H), 9.31 (H_{PP'''''''''''''''''''}, 1H), 9.32 (H_{QQ'''''''''''''''''''}, 1H), 9.33 (H_{RR'''''''''''''''''''}, 1H), 9.34 (H_{SS'''''''''''''''''''}, 1H), 9.35 (H_{TT'''''''''''''''''''}, 1H), 9.36 (H_{UU'''''''''''''''''''}, 1H), 9.37 (H_{VV'''''''''''''''''''}, 1H), 9.38 (H_{WW'''''''''''''''''''}, 1H), 9.39 (H_{XX'''''''''''''''''''}, 1H), 9.40 (H_{YY'''''''''''''''''''}, 1H), 9.41 (H_{ZZ'''''''''''''''''''}, 1H), 9.42 (H_{AA''''''''''''''''''''}, 1H), 9.43 (H_{BB''''''''''''''''''''}, 1H), 9.44 (H_{CC''''''''''''''''''''}, 1H), 9.45 (H_{DD''''''''''''''''''''}, 1H), 9.46 (H_{EE''''''''''''''''''''}, 1H), 9.47 (H_{FF''''''''''''''''''''}, 1H), 9.48 (H_{GG''''''''''''''''''''}, 1H), 9.49 (H_{HH''''''''''''''''''''}, 1H), 9.50 (H_{II''''''''''''''''''''}, 1H), 9.51 (H_{JJ''''''''''''''''''''}, 1H

4-Iodo-1,1,2,2,3,3,6,6-octafluoro[1,3]dioxacyclophane (14), from an aqueous solution (100 mL) of potassium iodide (31.5 g, 100mmol) was added the dicarboxylate solution previously prepared under nitrogen during. The mixture was kept at r.t overnight. The precipitated product was filtered and chromatographed.

(benzenetriol-carbonate (9)) is put (9) (0.40) 4-iodo-1,1,2,2,3,3,6,6-octafluoro[1,3]dioxacyclophane (14) (7.40g, 10% from 13) (mp 100-111 °C) ¹H NMR (D₂O, TMS, δ , $\text{J} = 8.40$ Hz, (H₂), 7.404 (s, 1H), 7.408 (s, 2H (m, (H₂), ¹⁹F NMR (DMSO-*d*₆) (H₂, $\text{J} = 244.41$ Hz, (H₂) -1.11 (s, 6H), $\text{J} = 244.41$ Hz, (H₂), -0.11 (2T (s), $\text{J} = 2.17$ (d Hz, (H₂) - 1.02 (s) (s), $\text{J} = 2.17$ (d Hz, (H₂), -0.16 (s) (s), $\text{J} = 2.07$ (d Hz, (H₂) -1.16 (s) (s), $\text{J} = 2.17$ (d Hz, (H₂) -1.03 (s) (s), $\text{J} = 2.07$ (d Hz, (H₂) -1.16 (s) (s), $\text{J} = 2.07$ (d Hz, (H₂).

Typical procedure for the coupling reaction of 14 in the presence of Cu powder (in a 100 mL, three-necked round bottomed flask containing 20 mL DMSO was added a mixture of iodo-oligo (3 g, 10.4 mmol), Cu powder (2g, 20.8 mmol). The mixture was heated at 120 – 140 °C) and stirred under N₂ atmosphere for 1 hrs, after the reaction was cooled to r.t. and 100 mL Et₂O was added. The mixture was filtered to remove the solids, and then washed with hexa (3 x 20 mL) and dried over Na₂SO₄. After removing the solvent by rotary evaporation, the residue was subjected to chromatography (silica gel) using hexane/EtOAc (10:90) as eluent to obtain pure hexa-oligo (3) (3g, 40%) as a 1:1 mixture of di and mono isomers, as confirmed by ¹⁹F NMR.

(Hexa-oligo (3)) 4-iodo-1,1,2,2,3,3,6,6-octafluoro[1,3]dioxacyclophane (14) (7.40 g, 10mmol) ¹H NMR (D₂O, TMS, δ , $\text{J} = 8.40$ Hz, (H₂), 7.404 (s, 1H), 7.408 (s, 2H (m, (H₂), 7.40 (s, 1H), 7.404 (s, 2H (m, (H₂), ¹⁹F NMR (DMSO-*d*₆) (H₂, $\text{J} = 244.41$ Hz, (H₂) -1.11 (s, 6H), $\text{J} = 244.41$ Hz, (H₂), -0.11 (2T (s), $\text{J} = 2.17$ (d Hz, (H₂) - 1.02 (s) (s), $\text{J} = 2.17$ (d Hz, (H₂) -0.16 (s) (s), $\text{J} = 2.07$ (d Hz, (H₂) -1.16 (s) (s), $\text{J} = 2.17$ (d Hz, (H₂) -1.03 (s) (s), $\text{J} = 2.07$ (d Hz, (H₂).

(H₂) ¹⁹F NMR (4-100 MHz) (d, ¹J = 146.85 Hz, (H₂) -133.994 (d, ¹J = 246.25 Hz, (H₂) -134.333 (d, ¹J = 127.36 Hz, (H₂) -113.628 (d, ¹J = 223.86 Hz, (H₂) (d₂) = 0.282

Pseudo-*n*-fluoro-1,1,1,2,3,4,5,6,10-octafluoro(2,2)paracyclophane ¹⁷ (1.0 g, 2.944 mmol) mp 113-115 °C. ¹H NMR (CDCl₃) 8.075 (s, 1H), 7.877 (m, 2H), ¹⁹F NMR (4-100 MHz) (d, ¹J = 144.79 Hz, (H₂) -113.255 (d, ¹J = 244.79 Hz, (H₂) -134.439 (d, ¹J = 242.44 Hz, (H₂) -133.242 (d, ¹J = 242.44 Hz, (F) MS m/z 442 (M⁺) (99%), 133 (100). The combined yield of the three diastereoisomers is 97%.

Pseudo-*n*-fluoro-1,1,1,2,3,4,5,6,10-octafluoro(1,2)paracyclophane ¹⁸ (recrystallized pseudo-*n*-fluoro-1,1,1,2,3,4,5,6,10-octafluoro(2,2)paracyclophane (1.30 g, 3.84 mmol) in chloroform (3.0 mL, 50 mL) was stirred for 1 h at room temperature, iron powder (3.00 g, 31.71 mmol) was added, and the reaction mixture was heated to reflux. Concentrated hydrochloric acid (7 mL) was added dropwise to the mixture, and reflux was continued for 4 h. After this time, the mixture was cooled to room temperature and was added to ice water (200 mL). The solids then produced were filtered and redissolved in chloroform. This chloroform solution was filtered and evaporated, and the solid residue was chromatographed (chloroform) to give (d₂) = 0.47) pseudo-*n*-fluoro-1,1,1,2,3,4,5,6,10-octafluoro(2,2)paracyclophane (0.91 g, 82%) mp 211 °C (dec). ¹H NMR (CDCl₃) 8.109 (d, ¹J = 0.40 Hz, 1H), 8.103 (s, 1H), 8.341 (d, ¹J = 0.40 Hz, 1H), ¹⁹F NMR (4-100 MHz) (d, ¹J = 233.54, ¹J = 0.40 Hz, (H₂) -134.370 (d, ¹J = 233.54 Hz, (H₂) -136.873 (d, ¹J = 242.44, ¹J = 0.40 Hz, (H₂) -113.223 (d, ¹J = 242.44 Hz, (F₂) MS m/z 382 (M⁺, 100%), 133 (100).

An ethereal solution with a 1:1 mixture of pseudo-*m*- and pseudo-*p*-diastere-1,1,1,2,3,4,5,6,10,10-octachloro-2,2[paracyclophane] gave the corresponding pseudo-*m*- and pseudo-*para*-diastere-1,1,1,2,3,4,5,6,10-octachloro-2,2[paracyclophane] in 84% yield (transacetalization (7), $R_2 = \text{O} \cdot \text{H}$). Anal. Calcd for $\text{C}_{14}\text{H}_2\text{Cl}_8\text{O}_2$: C, 30.39; H, 1.42; Cl, 51.11. Found: C, 30.69; H, 1.35; Cl, 50.97. MS m/z 382 (M^+ , 1.7%), 176 (100%) as ^{18}O NMR (CDCl_3) δ^{H} 5.66 (d, $^1J = 8.40$ Hz, 4H), 5.44 (d, $^1J = 8.40$ Hz, 4H), 4.04 (s, 4H), ^{19}F NMR (4:1 H_2O : CDCl_3) δ^{F} -112.468 (d, $^1J = 204.21$ Hz, 1F), -108.401 (d, $^1J = 214.25$ Hz, 1F), -107.844 (d, $^1J = 8.40$ Hz, 4H), 4.04 (d, $^1J = 8.40$ Hz, 4H), 4.00 (s, 4H), ^{19}F NMR (8:1 H_2O : CDCl_3) δ^{F} -204.11 Hz, 1F), -109.045 (d, $^1J = 209.32$ Hz, 1F), -108.342 (d, $^1J = 204.21$ Hz, 1F), -108.401 (d, $^1J = 214.25$ Hz, 1F).

Typical Desacetalization Procedure. A solution of pseudo-*m*-diastere-1,1,1,2,3,4,5,6,10,10-octachloro-2,2[paracyclophane] (2.05 g, 5.24 mmol) in water and (4 mL) was cooled to 0°C in an ice/water bath, and HCl (2 N, 1.5 mL) were carefully added (with stirring) and ensuring the temperature was still below 5°C , sodium acetate (2.93 g, 28.70 mmol) in 1 mL H_2O was added dropwise. The reaction was stirred at the temperature for 1 h and then used for the following transformation.

Pseudo-*m*-diastere-1,1,1,2,3,4,5,6,10,10-octachloro-2,2[paracyclophane]. Into an aqueous solution (10 mL) of potassium acetate (3.11 g, 30.76 mmol) was added the prepared desacetalization solution slowly with stirring. The mixture was kept at room temperature overnight. The precipitated product was filtered and chromatographed (hexane/ether 9/1) to give ($R_2 = \text{O} \cdot \text{H}$) pseudo-*m*-diastere-1,1,1,2,3,4,5,6,10-

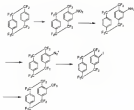
then heated to 50-60 °C gradually and kept at that temperature for 1 hr. ¹⁹F NMR showed the reaction was over. Poured the reaction mixture into 10 mL Et₂O. The resulting solution was washed with 5% HCl(aq.) x 10 mL, then brine 2 x 10 mL. The organic layer was dried over CaCl₂. After the organic solvent was evaporated, the solid was subject to column chromatography (eluent: EtOAc:n-C₄H₁₀ = 1:8). pure-product was obtained in 71% yield. ¹⁹F NMR δ: -101.71 (20H 4-Br, 2F), -110.73 (20H 10Br, 2F), -114.19 (22H 6, 4-Br, 2F), -114.22-14.154 (2H 2Br, 2F) ppm. ¹H NMR: 7.09-7.73 (m) ppm. IR (KBr solid, 400-1000, broad 3300-3500).

CHAPTER 1 SYNTHESIS AND REACTIVITY OF A NOVEL DOMERIC DERIVATIVE OF AF4: A NEW SOURCE OF TRIFLUOROMETHYL RADICALS

1.1 Introduction

In chapter 1 we discussed about the synthesis of AF4 and some *afix*-derivatives. Zinc proved to be the best reducing agent for the synthesis of AF4 from TFPX dichloride, but when other TFPX-dichloride derivatives were applied to the similar reaction conditions, the yields dropped significantly, and some dichlorides just gave complex mixtures, with no AF4 derivative being isolated.

Because ring-substituted derivatives of AF4 have the potential to produce *payless* films with enhanced properties, efforts have been directed at the synthesis of compounds such as trifluoromethyl derivative 66. Although 66 has been prepared by a traditional linear step synthesis sequence beginning with the state of AF4²⁰



Scheme 1

A more direct method based on Kuroda's free radical polymerization methodology appeared potentially attractive (Scheme 2).³⁰

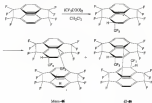


(polymers of *m*, *p*, *o* were discussed)

Scheme 2

3.2. Preparation of Tetrafluoromethylated AP4 from AP4

However, when tetrafluoromethyl peroxide was allowed to decompose in the presence of AP4 in refluxing CH_2Cl_2 , although the tetrafluoromethyl radical added to one of the imine rings of AP4, no monomeric to-td was observed. Instead, the intermediate tetrafluoromethyl radical **48**, proved to be excessively stable, so stable that it survived sufficiently long as to dimerize to a 50:50 mixture of the novel and structurally unprecedented dimerization products, *trans*-**48** and *cis*-**48** in a total yield of 50%.¹⁸



Scheme 3

X-ray structures and structural analysis of *trans*-**48** and *cis*-**48** are listed in Figures

S. 3 and tables 1 and 2.

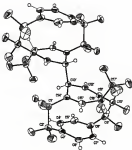


Figure 8. Percentage rates (SDTTP) of injury due

Table 1 Crystal Data and Structure Refinement^a

chemical formula	Al_2SiO_5	FeSiO_3
empirical formula	$\text{C}_{12}\text{H}_{10}\text{FeO}_{12}$	$\text{C}_{12}\text{H}_{10}\text{SiO}_{12}$
formula weight	500.50	500.50
temperature	1100(2) K	1100(2) K
wavelength	0.710 73 Å	0.710 73 Å
crystal system	orthorhombic	orthorhombic
a (Å)	7.581(8)	7.581
b (Å)	$a = 9.0134(1)$ Å $b =$ $11.4014(2)$ Å $c =$ $19.2278(2)$ Å	$a = 11.0014(1)$ Å $b =$ $11.1004(2)$ Å $c =$ $19.2404(2)$ Å
c (Å)	19.2278(2)	19.2404(2)
β (°)	90°	90°
γ (°)	90°	90°
volume, V (Å ³)	1299.79(2), $Z = 4$	1299.79(2), $Z = 4$
density (calc)	1.7018 Mg m ⁻³	1.7018 Mg m ⁻³
absorption coefficient	0.752 mm ⁻¹	0.708 mm ⁻¹
$F(000)$	1420	700
crystal size	0.75 × 0.71 × 0.11 mm ³	0.71 × 0.70 × 0.37 mm ³
range for data collection	1.01–27.36°	1.95–24.95°
reflections collected	23 762	36 700
independent reflections	7611 [$R_{\text{int}} = 0.0247$]	9011 [$R_{\text{int}} = 0.0140$]
completeness to θ	97.86% (99.75%)	94.96% (98.15%)
absorption correction	integration	applied
max and min transmission	0.9401, 0.5034	0.8111, 0.0177
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	15 715/0/14	19 010/0/14
goodness-of-fit on F^2	1.000	1.000
final R indices [$R = wR$]	$R_1 = 0.0194$, $wR_2 =$ 0.0479 [0.0246]	$R_1 = 0.0144$, $wR_2 =$ 0.0303 [0.0175]
R indices (all data)	$R_1 = 0.0123$, $wR_2 =$ 0.0308	$R_1 = 0.0088$, $wR_2 =$ 0.0176
extinction coefficient	0.0079(4)	0.006(3) (9)
largest diff peak and hole	0.280 and -0.240 e Å ⁻³	0.292 and -0.211 e Å ⁻³

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, wR_2 = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}, R = \sum |F_o - F_c| / \sum |F_o|,$$

$$R^2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}, w = 1/[\sigma^2(F_o^2) + (0.0070P)^2 + 0.11P], \text{ where } P = [\max(F_o^2, R_1) + 2A]/3$$

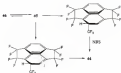
Table 2. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg)^a

d1-48	
C1-C7	1.375(2)
C1-C12	1.381(2)
C4-C7-C1	180°
C1-C7-C12	180°
C1-C7-C12a	-88.8(2)
C1-C7-C7a	87.8(2)
d10-48	
C1-C12	1.382(5)
C12-C13-C14	108.4(5)
C12-C13-C13B-C14B	-17.8(5)
C13-C14	1.373(5)
C13-C14-C14a	180°
C13-C14-C14B-C13B	-16.3(5)

^a Symmetry transformations used to generate equivalent atoms: #1: $x+1, y+1, z$

#2: $-x+1, y+1, z+1$

Not surprisingly, the new C-C bond in **48** that was formed as a result of joining the two radical fragments, proved to be quite weak, with bond dissociation energy homolysis to regenerate radical **48a** temperatures above 150 °C. Thus, when a 0.1 M solution of pure **d1-48** in acetonitrile was heated to 170 °C in the presence of 1.5 M 1,4-cyclohexadiene, radical **48** was trapped quantitatively by H transfer to form dihydro product **49**, with no concomitant isomerization to **isomer-48** being observed. In contrast, when **d1-48** was similarly heated in the presence of 0.45 M I_2 , isomerization to **isomer-48** was observed to be competitive with trapping of **48** by I_2 to form a nonisolated, but presumed intermediate product, **48'**, which rapidly loses H_2 to produce the macrocyclic C71-substituted NPA derivative, **44**. Such results indicate clearly that homolysis of **48** occurs, with isomerization being competitive with atom transfer.



Scheme 4

Since the thermolysis of **44** in the presence of 1,4-CDS appeared to involve rate-determining homolysis of **44** to form two radicals, **45**, the kinetics for the process for the two diastereomers of **44** were studied, each ester being determined at five temperatures for each, and the activation parameters for both systems were calculated and given in Table 3. The weak C-C bonds represented by these E_a 's derive from a combination of delocalization and B-ring strain effects, and they are consistent with their long bond lengths (1.583 Å, for *trans*-**44**).

Table 3 Rate Constants (k) for Homolysis of *trans*- and *cis*-**44**

T/°C	<i>trans</i> - 44	<i>cis</i> - 44	<i>trans</i> - 44	<i>cis</i> - 44	<i>trans</i> - 44
k_{hom}	9.7×10^{-7}	1.6×10^{-6}	6.5×10^{-6}	1.0×10^{-6}	1.1×10^{-6}
k_a	6.9×10^{-7}	1.3×10^{-6}	5.4×10^{-6}	6.7×10^{-6}	1.1×10^{-6}

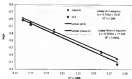


Figure 3. Arrhenius plots of the kinetic data for mono- and di-46

Table 4. Activation Parameters for Homolysis of mono- and di-46

Compound	$\log A$	E_a^{cal}	$\Delta H^\ddagger_{\text{cal}}$	$\Delta S^\ddagger_{\text{cal}}$	$\Delta G^\ddagger_{\text{cal}}$
mono-46	17.2 ± 0.8	42.4 ± 1.9	43.8	18	74.7
di-46	18.2 ± 1.3	44.8 ± 3.0	45.8	22	74.9

^a In toluene; ^b $T = 177.8 \text{ }^\circ\text{C}$; ^c in solid state

Notably, both isomers of 46 were found to be highly resistant to oxidative or dehydrogenative aromatization procedures (DIBAL-HCl, or $\text{P}(\text{BuO})_3/\text{Cu}$) that would have been a novel $\text{In}(\text{I})$ photocyclophane. Neither electron transfer nor H-atom transfer from 46 were productive, the former because of 46's electron deficiency, and the latter because of the steric accessibility of either of the two Br atoms that must be removed from treatment with N-bromosuccinimide (NBS, reflux, 48 h) left 46 untouched. (In

contrast, similar treatment of dihydro-product with HBr led to an smooth, quantitative conversion to **44**.)

Unexpectedly when simply heated to $170\text{ }^{\circ}\text{C}$ in the absence of a suitable azobisisobutyrate agent, both **43**- and **meso-44** underwent quantitative conversion to two-molecules of **44**, along with potential equivalent of two CF_3 radicals. Evidently this process did indeed involve the generation of free- CF_3 radicals was obtained by carrying out the thermolysis in benzene solution, with the result that trifluoromethylbenzene was formed, much as was observed by Sawada in his study of the reactions of $(\text{CF}_3)_2\text{C}=\text{C}=\text{C}_2$ with benzene.²⁸

Close sources of CF_3 radicals are quite rare. The aromatic-like "peroxide" radical, $(\text{CF}_3)_2\dot{\text{C}}-\text{C}(\text{F})_2\dot{\text{C}}_2$ known as Scherer's radical is such a source.²⁹ It is known to slowly and cleanly fragment to generate CF_3 radicals at $100\text{ }^{\circ}\text{C}$. Probably the most commonly used source of CF_3 radicals, as mentioned above, is $(\text{CF}_3)_2\text{C}=\text{C}=\text{C}_2$, but it is potentially hazardous, thermally unstable peroxide that decomposes slowly at room temperature (half-life is ca. $50\text{ }^{\circ}\text{C}$)^{30,31} In contrast, **meso**- and **43-44** are symmetrical compounds, stable indefinitely at room temperature, but remarkably capable of safely and quantitatively^{32,33} generating CF_3 radicals at temperatures of $>150\text{ }^{\circ}\text{C}$, with the only side product being the effectively inert **44**. Among other possible applications, **meso**- and **43-44** appear to have potential utility as high-temperature, free-radical initiators of polymerization.

Table 1 Polymerization of YDF Using Initiator 44-46: Experimental Conditions and Results

[YDF] ₀ /[46] ₀	T / °C	t / h	YDF, % conversion	DP _n , by ¹ H NMR	% normal YDF Units ^a
1/4	174 (slow mix)	15.5 (slow mix)	55	220 ± 15	93.8
2/3	174	14	35	28 ± 3	93.3
1/4	174	14	67	114 ± 8	90.7

^a "Normal" YDF units are those found in head-to-tail (-CH₂-CF₂-CH₂-CF₂-) sequences (as opposed to head-to-head (-CH₂-CF₂-CF₂-CH₂-) sequences.)

One could assess the degree of chaining of the macromolecular chain, using the following ratio of integrals: % defect = $(I_4 + I_5)/(I_1 + I_2)$. The observed proportion of defect (3.3-4.7%) is surprisingly small for experiments performed at 170-180 °C. Values of the reversed YDF defect are reported to range between 5 and 75,⁷⁰ although these are values as low as 3.4% reported under Ziegler-Natta conditions at temperatures below room temperature.^{71,72}

Although requiring high temperatures, the above polymerizations of YDF using initiator 44 leads to highly narrow PDI's with CF₂ end groups which often imply deactivation of the degree of polymerization. Furthermore, such CF₂ end groups could lead to polymers with novel properties.

In summary, novel radical initiation chemistry of AIB leads to formation of an unprecedented new class of linear CF₂-substituted AIB derivatives. These highly sterically constrained compounds undergo clean two-step thermal homolysis processes to form trifluoromethyl radicals in a process that is amenable to their use as free radical initiators, as is shown by a study of the polymerization of vinylbenzotrifluoride.

3.3 Experimental Section

Synthesis of Trifluoromethyl Radical with 4-F Into a 100-mL three-necked, round-bottomed flask was added a mixture of $\text{NFl} \cdot$ (5 g, 38 mmol), acetylene dichloride (40 mL), and $\text{HgCl}_2 \cdot (2\text{O})_2$ (1.1 g, 38 mmol). The mixture was cooled to -40°C and under vigorous stirring, $(\text{CF}_3\text{COO})_2\text{O}$ (1.1 g, 38 mmol) was slowly added. After the addition was complete, the mixture was allowed to slowly warm to room temperature and then heated to reflux for 12 h. The product precipitated during this time. After cooling to 0°C , the crude product was obtained by filtration. Recrystallization from acetylene dichloride gave pure product **4f** (3.1 g, 30%) as a 17:3 mixture of diastereomers (as determined by ^{19}F NMR). Separation of diastereomers, *4f*¹ and *trans-4f*², was obtained by recrystallization from ethyl acetate, wherein each diastereomer gave different shaped crystals, which could be separated by picking out each one manually. Crystals obtained in this manner were used for the X-ray analysis, which confirmed that the major isomer was the *4f*¹.

^{19}F NMR for *trans-4f*²: 4.44 (t, 2H, CF_3 , -109.1 (AM, $J = 342.9$ Hz, $2F_2$), -118.71 (AM, $J = 344.9$ Hz, $2F_1$), -112.45 (AB, $J = 343.6$ Hz, $2F_3$), -112.92 (AB, $J = 344.4$ Hz, $2F_4$), -103.82 (AM, $J = 60.8$ Hz, $2F_5$), -114.93 (AB, $J = 344.9$ Hz, $2F_6$), -116.32 (AB, $J = 342.84$ Hz, $2F_7$), -116.62 (AB, $J = 342.9$ Hz, $2F_8$) ppm; ^1H NMR (400 MHz, CDCl_3) δ : 7.76 (m, $J = 9.0$ Hz), δ : 7.54 (d, 4 H, $2H_2$, δ : 7.35 (d, $2H_2$), 7.30 (AM, $J = 8.18$ Hz, $2H_3$), 7.49 (AM, $J = 8.14$ Hz, $2H_4$), 7.73 (AB, $J = 8.4$ Hz, $2H_5$), 7.64 (AB, $J = 8.1$ Hz, $2H_6$).

¹³C NMR for **47-48**: 8.44 (s, 4H), -0.02 (s, 4H), J = 144.3 Hz, 2P₁, -0.01 (s, 4H, J = 144.3 Hz, 2P₂), -0.01 (s, 4H, J = 144.3 Hz, 2P₃), -0.01 (s, 4H, J = 144.3 Hz, 2P₄), -1.17 (t, 4H, J = 14.4), 1.44 (s, 6H, 2P₅), -1.14 (s, 4H, J = 128.7 Hz, 2P₆), -0.14 (s, 4H, J = 128.7 Hz, 2P₇), -0.06 (s, 4H, J = 128.7, 2, 8 Hz, 2P₈), 1.14 (s, 4H, J = 128.7 Hz, 2P₉) ppm. ¹³C NMR for **49**: 81.00 (s, 2H), 3.79 (q, J = 8.4 Hz, 2H), 4.17 (q, 2.2 Hz, 2H), 6.25 (q, 2H), 7.47 (AB, J = 8.16 Hz, 2H), 7.67 (AB, J = 8.4 Hz, 2H), 7.73 (AB, J = 8.4 Hz, 2H), 7.80 (AB, J = 8.1 Hz, 2H).

Kinetic Experiments: Ether was in **47-48** (5.2 mg, 0.16 × 10⁻³ mmol) was added to an NMR tube containing 8.3 mL of CD₃CN and 0.3 mL of 1,1-dichloroethane. After the tube was degassed in vacuum for 5 min at -78 °C, the NMR tube was immersed in a constant temperature bath for an appropriate time, then removed, sealed, and analyzed by ¹³C NMR, with the concentration of **48** being measured versus internal standard, trifluoromethylbenzene. In this manner were rates determined for the formation of each product at five different temperatures, with the observed rate constants being given in Table 3, and plots of the data being shown in Figure 3.

Reaction of **47-48 with **5**:** Into an NMR tube was added a mixture of 0.5 mL of CD₃CN, **5** (0.1 g, 0.04 mmol) and **47-48** (1 mg, 0.16 × 10⁻³ mmol). The NMR tube was degassed for 5 min under vacuum (0.4 mm Hg) at -78 °C. After the tube was sealed, it was immersed in a constant temperature bath maintained at 115 °C and the reaction monitored for 1 h. The ¹³C NMR spectrum of the solution indicated that both **48** and **mono-48** were formed from **47-48**. When allowed to go to completion (monitored heating for 24 h), the reaction produced an 87% yield of **44** as the only detectable product. ¹³C

NOESY: 7.693 (s, 1H), 7.623 (s, 2H), 7.534 (d, $^3J = 8.40$ Hz, 1H), 7.504 (d, $^3J = 8.40$ Hz, 1H), 7.364 (d, $^3J = 8.40$ Hz), 1H), 7.329 (d, $^3J = 8.40$ Hz, 1H), ^{19}F NMR: δ = -108.236 (dd, $^3J = 242.16$, $^2J = 7.26$ Hz, 1F), -113.228 (dd, $^3J = 242.16$, $^2J = 29.67$ Hz, 1F), -113.411 (dd, $^3J = 242.16$, $^2J = 12.14$ Hz, 1F), -114.823 (dd, $^3J = 231.16$, $^2J = 2.67$ Hz, 1F), -114.877 (d, $^3J = 146.79$ Hz, 1F), -116.189 (dd, $^3J = 244.73$, $^2J = 4.81$ Hz, 1F), -117.449 (d, $^3J = 237.58$ Hz, 1F), -117.623 (dd, $^3J = 237.56$, $^2J = 4.84$ Hz, 1F), 145.466 (d, 126.3, 124.4 (C), 126 (C=O).

Attempted Acetylation of 8b. Refluxing 4b with CCl_4 in EtOAc led to recovery of starting material, as did attempted bromination with NBS in refluxing CCl_4 , and attempted oxidation by Et_3COH . Heating with PAC at refluxing volume led to formation of a complex mixture of products.

Polymerizations. Bulk polymerizations of VDF (locally donated by Solvay S. A., Belgium) were performed in thick borosilicate Carius tubes in a batch process (length, 130 cm; internal diameter: 18 mm; thickness, 2.5 mm; for a total volume of 6 cm³). After the initiator was added, the tube was connected to a vacuum line and purged several times by evacuating and flushing with helium. After five three-beam cycles at least, to get rid of oxygen, VDF was trapped under vacuum in the tube frozen in liquid nitrogen, after its release from an intermediate smaller container calibrated in pressure. The required amount of VDF (2.758 $\pm$ 0.003 g) introduced into the tube was obtained by the minute drop of pressure in the release container, initially fed by a cylinder of 500 g of VDF. A beforehand calibration gave a weight of trapped VDF (in g) versus drop of pressure (in

lar)-was determined (for 0.75 g of VLP – a difference in pressure of 0.50 bar being required)

The tube, under vacuum and contained in liquid nitrogen, was sealed and placed for the required time into the study of a shaking oven at the required temperature.

X-ray Experiments. Data were collected at 111 K on a Siemens Smart Platform equipped with a CCD area detector and a graphite monochromator utilizing Mo K α radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using up to 3052 reflections. A hemisphere of data (1381 frames) was collected using the ω -scan method (0.3° frame width). The first 50 frames were discarded at the end of data collection to monitor instrument and crystal stability (maximum variation ω/ω was <7%). Empirical absorption corrections were applied based on the entire data set.

For mono-46: $C_{12}H_{10}P_{12}O$, $M_r = 560.58$ (molar), P_1 , $a = 11.8034(3)$ Å, $b = 12.1614(3)$ Å, $c = 15.9039(3)$ Å, $\alpha = 74.872(1)^\circ$, $\beta = 76.421(1)^\circ$, $\gamma = 63.454(1)^\circ$, $V = 1321.48(2)$ Å 3 , $Z = 2$, $D_{\text{calc}} = 0.771$ g cm $^{-3}$, Mo K α ($\lambda = 0.71073$ Å, $T = 111$ K).

For di-46: $C_{12}H_{10}P_{12}O$, $M_r = 560.58$ (molar), $P_2(1)$, $a = 8.6424(1)$ Å, $b = 13.4714(2)$ Å, $c = 29.2213(2)$ Å, $\beta = 94.354(1)^\circ$, $V = 3248.73(2)$ Å 3 , $Z = 4$, $D_{\text{calc}} = 1.766$ g cm $^{-3}$, Mo K α ($\lambda = 0.71073$ Å, $T = 111$ K).

The structures were solved by the Direct Methods in SHELXTL 20 and refined using full-matrix least squares, and the structural data are given in Tables 4 and 5. The ORTEP drawings of mono- and di-46 are given in Figures 2 and 3, respectively. The non-

H atoms were treated isotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. For *mon-66* a total of 138 parameters were refined in the final cycle of refinement using 4547 reflections with $I > 3\sigma(I)$ as yield R_1 and wR_2 of 7.88 and 19.87%, respectively. For *di-66*, a total of 140 parameters were refined in the final cycle of refinement using 1204 reflections with $I > 3\sigma(I)$ as yield R_1 and wR_2 of 7.74 and 19.79%, respectively. Refinement was done using P^3 .

CHAPTER 4

UNEXPECTED ONE-STEP SYNTHESIS OF 1,1,2,2,3,3,10,10-OCTAFLUORO- [1,2,3,4,5,6,7,8,9,10]-NONACYCLOPENTANE-4,7-DIOL AND ITS PROPERTIES

4.1 Introduction

The synthesis of **AP4** (**2**) derivatives, especially halogenated **AP4**, has been discussed in detail in the previous chapters. Due to the high reactivity of fluoro-1,1,2,2,3,3,10,10-octafluoro[2,2]paracyclophane (reba-**AP4**),¹⁶⁻¹⁷ it would be valuable if **AP4** derivatives could be accomplished in one step starting from the more readily available **AP4**, even though the synthesis of reba-**AP4** was possible in four steps starting from **AP4**. **AP4** is more suitable for the reaction of moderately deactivated aromatic compounds due to the absence of perfluoroalkyl groups in the 1-4 positions of the benzene ring. By applying a strong electrophilic substitution system for deactivated aromatic compounds, substitution might occur for **AP4**. It was reported that $\text{I}_2/\text{HClO}_4/\text{H}_2\text{SO}_4$ ¹⁸ reacted with 1,4-bis(trifluoromethyl)benzene giving the corresponding iodinated products in good yield. Surprisingly when this system was applied to **AP4**, an analogue of **AP4** to 1,1,2,2,3,3,10,10-octafluoro[1,1]paracyclophane-4,7-diol (**44**) was found as the only observed reaction.

3.2 Results and discussion

Quinones have a higher redox-potential than the corresponding quinone monomers. Although oxidation of aromatic compounds is one of the many ways to synthesize quinones, only the condensed polyaromatic hydrocarbons have been reported to be oxidized to such quinones. Benzene itself has not been successfully oxidized to an 1,4-quinone, and the oxidation of toluene always gives a lot of side products.²¹

AP4, with two different aromatic rings has in fact, again very limited solubility. It was found that the oxidation of AP4 in TFA in the presence of HIO_3 was quite a clean reaction, giving **48** in 50% yield (Scheme 1).



Scheme 1

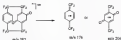
The presence of sulfuric acid was essential to the reaction. In its absence, no reaction occurred even if the reaction was heated to reflux for 24 hours. The TFA solvent also played an important role, even when the other solvents, e.g. AcOH, CH_2Cl_2 , $\text{CH}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ were used instead of TFA, the reaction did not occur.

The structure of the two benzene rings is very important for the solubility in water. When the so-called *trans* was subjected to the chemical reaction conditions, no reaction occurred, and only the starting material was recovered.



Scheme 1

The structure of the product *cis*-isomer was demonstrated based on MS, ^{19}F NMR, and IR NMR. The typical mass spectra of 2,3-cyclophane show that they fall apart to give the corresponding *para*-cations, which giving useful information on the substitution on the respective cyclophane. In this case, we observed three major peaks: *m/z* 176, 206 and 302.



Scheme 2

Due to the geometry of AP4, the two phenyl rings can not rotate freely, thus making the molecule rigid, and when the ring is substituted, it affects the entire molecule. Typically, for a mono-substituted AP4-compounds, the ^{19}F NMR will give 3 AB peaks, whereas a symmetrically bis-substituted AP4 with two identical substituents will give

four AB peaks. The ^1H NMR of our product gave 4 AB signals, which is typical of such bis-substituted AB $_2$ derivatives. The isolation of AB $_2$ could also give an ortho quartet instead of the para-bisomer. In the para isomer, H^a and H^b will couple to each other, thus giving two doublets. The coupling constants will be that of a typical para-substituted benzene, which is around 7 Hz. However in the ortho case 8.7 Hz and 8.6 couple with each other, the coupling constants will be much smaller. 3-30a.



Scheme 4

The ^1H NMR of our product showed one singlet (2H) and two doublets (2H each) with a coupling constant of 8.7 Hz. Thus the structure was assigned to be the para AB $_2$ isomer.

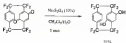
With the success of the isolation of AB $_2$, we tried to isolate via hydrocarbon analogues, but the reaction turned out to be a mess. (2,2)bisaryloxyphosphine itself can not be simply oxidized to its corresponding quinone. We also tried other electron deficient aromatic compounds without success. It seems that this isolation is unique for the AB $_2$ systems.

The related hydrocarbon cyclodimer species (AH) was first synthesized by Conn and his coworkers more than 20 years ago, with the total yield from the cyclodimer being less than 10%.



Scheme 5

Our AH species can be easily related to the corresponding hydroquinone form. The AH species was first dissolved in dichloromethane, and the resulting solution was treated with 10% Na_2O_2 (aq) with vigorous stirring. The reduction was complete in 1 minute (Scheme 6).



Scheme 6

Quinones have been widely used as oxidizing reagents²³. They also form charge transfer complexes with other electron rich species, such as hydroquinone and aryl ethers²⁴. When the AP4-quinone was allowed to mix with phenyl methyl ether, charge transfer complex was not observed to form in the solution, and no new peaks appeared in the UV spectrum. Similarly, when AP4-quinone and AP4-hydroquinone were mixed together, no charge transfer complex was found.

It was reported²⁵ that intramolecular charge transfer could be observed in the hydroquinone-quinone, and the expected low oxidative potential of AP4-quinone encouraged us to look into the possibility of the formation of charge transfer complexes. Similar to [2,2]paracyclophane-quinone, the AP4-quinone showed a new peak at 353 nm ($\epsilon = 110 \text{ cm}^2/\text{mol}$) in the UV spectra, and the new peak was similar to the charge transfer absorption. 1,1,2,2,3,3,4,4,4-Deafluoro[2,2]paracyclophane-4'-butyl-AP4-hydroquinone also showed an absorption at 358 nm which did not exist in the hydroquinone, the new peak may come from the formation of the intramolecular charge transfer complex.

4.3 Experimental Section

Typical procedure for the preparation of APH Quinone: Into a 50 mL of round-bottom flask was added a mixture of 10 mL THF, APH (3.5 g, 30 mmol), IBO_2 (2.5 g, 30 mmol) and Et_2SO_4 (10%) (2.5 g, 10% mmol). The reaction mixture was heated to reflux under stirring for 24 hrs. ^{19}F NMR showed all the APH was converted. After cooling to room temperature, the mixture was poured in 20 g crushed ice, a light yellow solid precipitated. After filtration, the solid was washed with hexane (pH = 7). The crude product was then subjected to flash chromatography (eluent: Hexane:AcOH) = (5 : 1 (v/v)). 1.2g pure APH quinone was obtained (yield: 32%).

^1H NMR, 300 MHz, CDCl_3 , 2.13(s, 2H), 2.74(s, 2H), 3.13(s, 2H), 3.76(s, 2H), 4.07 (s, 2H), 4.14-4.28 (m, 4 = 3H), 4.3 (t, 2H) -133.09 (s, 1 = 349.96(s, 2F) -138.29 (s, 344.95(s, 2F), -138.79 (s, 337.94(s, 2F) HRMS: Calcd for $\text{C}_{10}\text{H}_8\text{O}_2$, 160.0540, Found: 160.0541.

Preparation of APH hydroquinone: Into a 50 mL, round-bottom flask was added a mixture of CH_2Cl_2 (15 mL), APH quinone (1.5 g, 9 mmol), and 20 mL 2M Na_2SO_3 aq. solution. The reaction was vigorously stirred for 5 min at room temperature. After the reaction was finished, separated the organic layer, the water layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic solution was dried over Na_2SO_4 . After evaporating the solvent, the crude product was subjected flash chromatography (eluent: Hexane: AcOH) = 2 : 1 (v/v). Pure APH hydroquinone (1.75 g, 97%) was obtained.

¹H NMR, 5-6 ppm, 1H, 4.22 (s, 2H), 7.05 (d, 1H), 7.34, 7.44, 7.48, 7.54, 7.64, 7.67, 1H NMR, 8-11 ppm, 1 = 3.44 (s, 2H), -117.39 (d, 2 = 2.60 (s, 2H), -11.4 (d, 242.0 Hz, 2F), -11.5 (d, 242.0 Hz, 2F) 18545. Calcd for C₁₄H₁₀O₄, 242.027, Found 242.0423.

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BIOGRAPHICAL SKETCH

Jian-Jin Qian was born in 1960 in Huanan Province, People's Republic of China. He received his B.S. in Chemistry from Xiangtan University, Hunan, in 1980. In 1982 he obtained his master's Degree in Organoboron Chemistry under supervision of Professor Qing-Yun Chen from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. From 1982 to 1990 he worked as a synthetic-organoboron chemist in Professor Chen's research group. Then, from 1990 to 2000 he worked as a visiting scholar in Dr. William R. Dolbier, Jr.'s research group at the University of Florida. In the Spring of 2000 he entered the doctoral program in the Department of Chemistry, working with Dr. William R. Dolbier, Jr.'s group. Throughout his research activities he developed a number of good methods to synthesize APs, its precursors and derivatives. Upon completion of his doctoral studies, Qian looks forward to new chemical adventures at Genesoft Co. where he will begin work as a staff scientist.

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